



Acoustical Studies on Molecular interaction of 2'-Chloro-4-Methoxy-3-Nitro Benzilic acid with various Solvents at different concentrations using Ultrasonic technique

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Abstract: The ultrasonic velocity, density and viscosity have been measured for the binary mixtures of 2'chloro-4methoxy-3nitro benzilic acid (2C4MBA) with polar and non-polar solvents at 298K. The experimental data have been used to calculate the Density (ρ) and acoustical parameters namely, ultrasonic velocity (U), adiabatic compressibility (β), apparent molar volume (ϕ), acoustic impedance (Z), intermolecular free length (L_f), relative association (R_A). The excess values of some of the above parameters have also been evaluated. The above study is useful to discuss the nature and extent of solute – solvent interactions occurring in different solvents and in different concentrations at 298K.

Keywords: Ultrasonic velocity; Density; Excess parameters; Intermolecular hydrogen bonding.

1. Introduction

Study of intermolecular interaction plays an important role in development of molecular sciences. In recent years, ultrasonic technique has become a powerful tool in providing information regarding molecular behavior of liquids and solids owing to its ability of characterizing physicochemical behavior of the medium [1, 2]. A large number of Studies have been made on molecular interaction in liquid systems by various spectroscopic methods like Infrared spectra [3, 4], Raman effect [5, 6], Nuclear Magnetic resonance, ultra violet spectra [7] and other non spectroscopic techniques such as dielectric constant [8], ultrasonic velocity method [9, 10]. The rate of reactions and the stability of the intermediates formed depend on the intermolecular interactions of the medium. The intermolecular forces responsible for the molecular interactions can be classified as long range forces and Short range forces. The long range forces are the electrostatic induction and dispersion forces and they arise when the molecules come close enough together causing a significant overlap of electron clouds and are often highly directional. In the present work an attempt has been made to investigate the behavior of binary solutions of 2C4MBA in different polar and non polar solvents with regard to velocity, density, adiabatic compressibility, intermolecular free length from ultrasonic measurements using standard formulae at 298K. The components of these binary mixtures 2C4MBA and various solvents are interesting as they have proton donor as well as proton accepting ability. As a result, significant interaction through hydrogen bonding between unlike molecules in these binary mixtures is expected. The values of ultrasonic parameters at 298K are plotted against concentration and the graphs obtained are explained on the basis of the various intermolecular interactions present in the system and how the interactions are affected by the nature of solvents at different concentrations. The study of excess thermodynamic functions such as excess velocity, excess density, excess adiabatic compressibility, excess intermolecular free length, and excess viscosity are of

considerable interest in understanding the nature of intermolecular interactions in liquid mixtures [11]. Excess properties of binary liquid mixtures give more comprehensive information about the structural and interactional aspects of the liquid mixtures.

2. Experimental

2C4MBA was synthesised by crossed benzoin condensation followed by oxidation with Conc.HNO₃. Then benzil reacted with aq.KOH the driving force for the reaction is provided by the formation of a stable potassium benzilate followed by acidification. The structure of the compound was studied by IR, PMR, CMR and mass spectra. The molecular conformation was confirmed by single crystal XRD studies. Solvents like ethanol, acetonitrile, chloroform, acetone and 1, 4-Dioxane (s.d.fine,India,AR) were dried over molecular sieves. All the binary mixtures were prepared by mass in a dry box and were kept in special air tight bottles. Solutions of 2'-chloro-4-methoxy-3-nitro benzilic acid in the concentration range of 0.000938-0.03 mole% with different solvents were prepared at room temperature. The densities of pure liquids and binary mixtures were measured using a simple capillary pycnometer of bulb capacity $8 \times 10^{-6} \text{ m}^3$ with a graduated stem width of $5 \times 10^{-8} \text{ m}^3$ divisions (Systronics India, Ltd.). The marks on the capillary were calibrated using known densities of double distilled water. The accuracy of the density measurement was found to be $\pm 0.001 \text{ gm/cc}$. The viscosities of the binary mixtures were determined using an Ostwald Viscometer (Sigma Chemicals Instruments). The ultrasonic velocities of pure solvent and the binary mixtures were measured using a single crystal variable path interferometer at 2 MHz (Mittal Enterprises, New Delhi). The accuracy in ultrasonic velocity was found to be $\pm 0.05\%$. The temperature of the test liquids and their binary mixtures was maintained to an accuracy of ± 0.02 in an electrically controlled thermostatic water bath.

From the measured values of density ρ , viscosity η and ultrasonic velocity U , the adiabatic compressibility β or K_s , intermolecular free length L_f , relative association R_A and acoustic impedance Z , have been calculated using the following standard relations.

$$\beta = K_s = 1/u^2 \rho \quad (1)$$

$$L_f = K/u\rho^{1/2} \quad (2)$$

$$R_A = (\rho/\rho^\circ) \times (u^\circ/u)^{1/3} \quad (3)$$

$$Z = u\rho \quad (4)$$

where K is a temperature-dependent constant $(93.875+0.375 \times T) \times 10^{-8}$, T is the absolute temperature, Z is the acoustic impedance, K_s the adiabatic compressibility, L_f the intermolecular free length, R_A is the relative association, and ρ° , ρ , u° and u are the densities and ultrasonic velocities of the solvent and solution respectively.

3. Result and discussion

In the present investigation ultrasonic velocity measurement is used to assess the molecular interaction between 2C4MBA and different polar and non polar solvents. The values of ultrasonic velocities (u), densities (ρ), adiabatic compressibility (β or K), intermolecular free length (L_f) of 2C4MBA in different solvents and other acoustical parameters are given in Table 1.

Table A .1. Values of density, ρ ,ultrasonic velocity, u ,adiabatic compressibility, β ,intermolecular frelength, L_f , Relative Association R_A and excess functions of binary mixtures as a function of concentration (mole percent) using various solvents

Solvents	Concentration for various ultrasonic parameters					
	Velocity ms^{-1}					
Non-Ideal(NI)	0.000938	0.001875	0.00375	0.0075	0.015	0.03
Ethanol	1358	1854	1412	1274	705	885
Acetonitrile	1363	1220	1601	643	1224	1124
Acetone	470	480	460	490	475	480
Chloroform	1427	701	758	1132	1427	
1,4-dioxane	1492	1420	1400	1340	1406	1368

Non-Ideal(NI)	Density Kgm ⁻³					
Ethanol	790	767	667	768	773	772
Acetonitrile	754	747	770	750	775	760
Acetone	750	710	780	760	625	750
Chloroform	1440	1443	1445	1447	1450	
1,4-dioxane	1007	1017	1010	1006	1002	1009
Non-Ideal(NI)	Adiabatic compressibility Kg ⁻¹ ms ²					
Ethanol	6.8632	3.8412	6.3402	8.1753	2.5165	16.409
Acetonitrile	7.1558	8.9823	5.0629	3.2188	8.6126	1.0436
Acetone	60.359	69.553	60.588	54.801	70.914	57.870
Chloroform	3.3625	1.4658	1.2105	5.4574	3.4918	
1,4-dioxane	4.4610	4.9743	5.0515	5.5356	5.0484	5.2958
Non-Ideal(NI)	Intermolecular frelength A ⁰					
Ethanol	5.3895	4.0043	5.6351	5.8226	10.484	8.3572
Acetonitrile	5.4933	6.1627	4.6268	11.666	6.0345	6.6312
Acetone	10.010	10.956	9.4391	9.8142	13.165	10.001
Chloroform	3.8437	7.8189	7.2333	4.8427	3.8424	
1,4-dioxane	4.3435	4.5407	4.6215	4.8381	4.6202	4.7324
Non-Ideal(NI)	Relative Association (RA)					
Ethanol	0.8852	0.7170	0.7376	0.8791	1.0775	0.9976
Acetonitrile	0.9681	0.9953	0.9370	1.2367	1.0315	1.0405
Acetone	1.2374	1.2813	1.4931	1.6505	1.3660	1.1995
Chloroform	0.8717	1.1068	1.0800	0.9461	0.8777	
1,4-dioxane	1.0393	0.9983	1.0886	1.0385	0.8630	1.0321
Excess Velocity						
Ethanol	258.64	754.56	315.90	182.73	-366.01	-164.78
Acetonitrile	112.58	-28.080	353.97	-590.43	-3.520	-75.435
Acetone	2.0438	-17.089	-5.3627	27.564	19.207	36.209
Chloroform	461.73	-260.25	-199.32	178.73	475.90	
1,4-dioxane	129.60	60.278	45.473	-3.489	81.184	83.053
Excess Density						
Ethanol	-3.0452	-6.0082	-2.3456	-1.7805	15.940	6.7254
Acetonitrile	-1.2560	0.5741	-3.3651	23.615	0.3425	2.2151
Acetone	-2.6358	6.6423	-2.4056	-7.2895	9.3605	-1.4905
Chloroform	-3.9703	6.6752	4.6452	-1.8830	-3.6904	
1,4-dioxane	-0.8052	-0.2825	-0.1845	0.3356	-0.0632	0.3256
Excess Intermolecular free length						
Ethanol	-1.8008	-2.4587	-80.520	-5.8743	4.0525	2.0568
Acetonitrile	-0.4568	0.2047	-1.3025	5.6948	0.1784	0.8614
Acetone	8.358	9.208	7.7615	8.0874	11.245	8.0054
Chloroform	-1.7186	2.2355	1.6658	-0.6614	-1.5423	
1,4-dioxane	-0.3739	-0.1663	-0.0658	0.1854	0.0471	0.2854
Excess Acoustic Impedance						
Ethanol	0.1582	0.5075	0.0308	0.0713	-0.3454	-0.1885
Acetonitrile	0.0811	-0.0334	0.2887	-0.4514	0.0189	-0.0538
Acetone	0.3373	0.3366	0.3355	0.3333	0.3263	0.3194

Chloroform	0.6634	-0.3774	-0.2880	0.2595	0.6946	
1,4-dioxane	0.1169	0.0613	0.0365	-0.0180	0.0621	0.0741

The ultrasonic velocity is found to be the lowest at low concentration and the increase in ultrasonic velocity with increase in concentration is the expected trend [12]. Fig. 1 shows the plots of ultrasonic velocity versus mole fraction. It is evident from the values that ultrasonic velocity of benzilic acid increases with increase in concentration of polar solvent likes ethanol, acetonitrile and acetone. For polar solvents there is a sharp increase in velocity, reaching a maximum followed by a decrease.

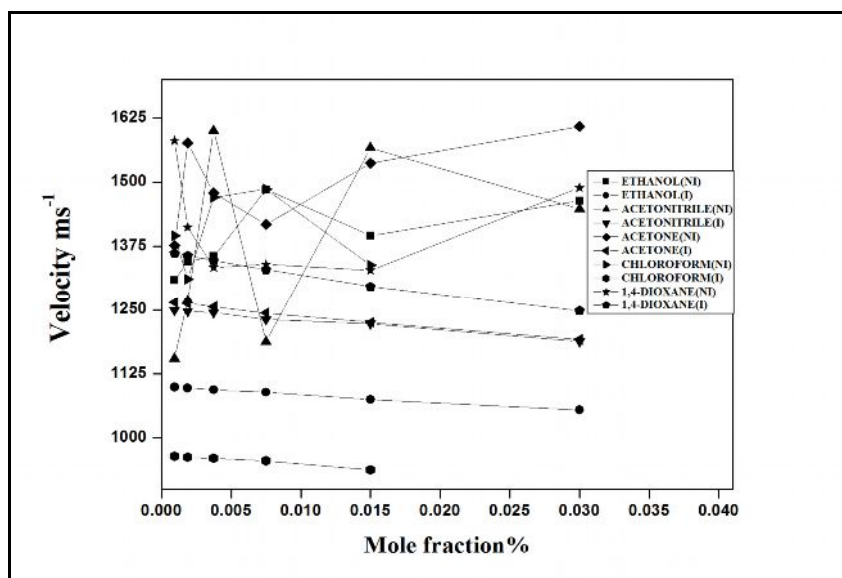


Fig. 1 Velocity (ms^{-1}) Vs Mole fraction% graph for 2'-chloro-4-methoxy-3-nitro benzilic acid in different solvents (shown in the inset)

The increase in ultrasonic velocity indicates that the interaction between ion and solvent is becoming more dominant. An opposite trend is observed in the adiabatic compressibility. A similar explanation for the decrease in compressibility with concentration of the liquid mixtures has been suggested by Fok and Moore [13]. The maximum in ultrasonic velocity is observed at 0.0075 mol% concentration. This is due to the replacement of weaker intermolecular attraction between solvent molecules by the strong intermolecular interactions. This indicates that the solvent-solvent interaction is replaced by solute-solvent interaction. For non polar solvents there is a decrease in velocity by increasing the concentration due to weak solvent - solute interactions.

Density is a measure of solvent-solvent and solute-solvent interactions. A decrease in the density of a solution with dilution is the expected trend [14, 15]. For the system of 2C4MBA and different solvents under study, there is a increase in density at low concentration region for polar solvents like ethanol, acetonitrile and there is an initial decrease in density (Fig. 2) for non-polar solvents viz chloroform. In the case of polar solvents, the increase in density is more significant. This can be attributed to the formation of intermolecular interactions between the solvent molecules by the addition of the solute which reaches a maximum. Increase in density with concentration is due to the shrinkage in the volume which in turn is due to the presence of solute molecules. In other words, the increase in density may be interpreted to the structure-maker of the solvent due the added solute. Similarly, the decrease in density with concentration indicates structure-breaker of the solvent. It may be also true that solvent-solvent interactions bring about a bonding, probably H-bonding between them. So, size of the resultant molecule increases and hence there will be decrease in density. In the case of ethanolic solutions, there is found to be a continuous increase in the density of the solution with an increase in concentration. This is attributed to the presence of strong intermolecular attraction such as dipole-dipole attraction and hydrogen bonding. In the case of acetonitrile the increase in concentration results in the preferential formation of intermolecular hydrogen bonding between the solute molecules, forming a well-arranged structure, leading to an increase in the volume of the solution, which leads to a decrease in density. An increase in concentration allows for a closer approach of solvent and solute molecules, and stronger association between solute and solvent molecules. Increase of density with concentration indicates the lesser magnitude of solute-solvent and solvent-solvent interactions. As the polarity of the solvent decreases, there is a decrease in

density. The initial sharp decrease in density can be explained on the basis of a sudden increase in the volume of the solution with the addition of 2C4MBA.

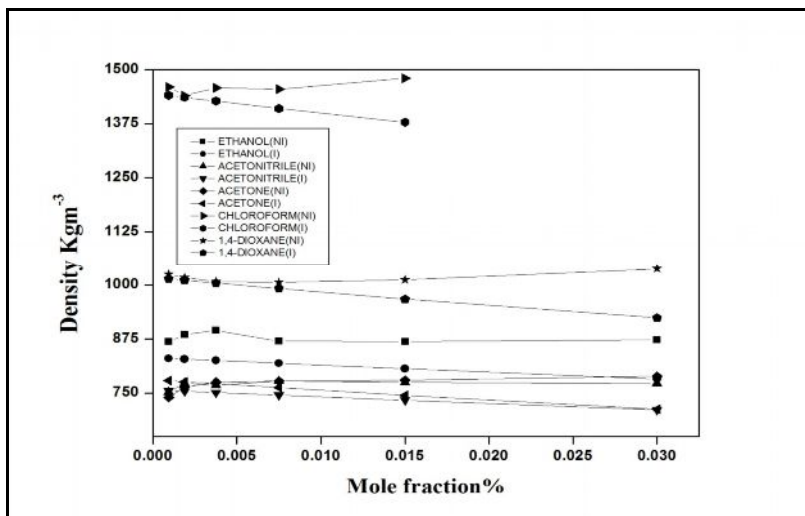


Fig. 2: Density (Kgm^{-3}) Vs Mole fraction% graph for 2'chloro-4methoxy-3nitro benzilic acid in different solvents (shown in the inset)

The adiabatic compressibility generally decreases with increase in concentration [12]. A high value of adiabatic compressibility for low concentration indicates a positive ion-solvent interaction, and at the same time the network of hydrogen bonding formed by the solvent molecules is not much disturbed (Fig. 4).

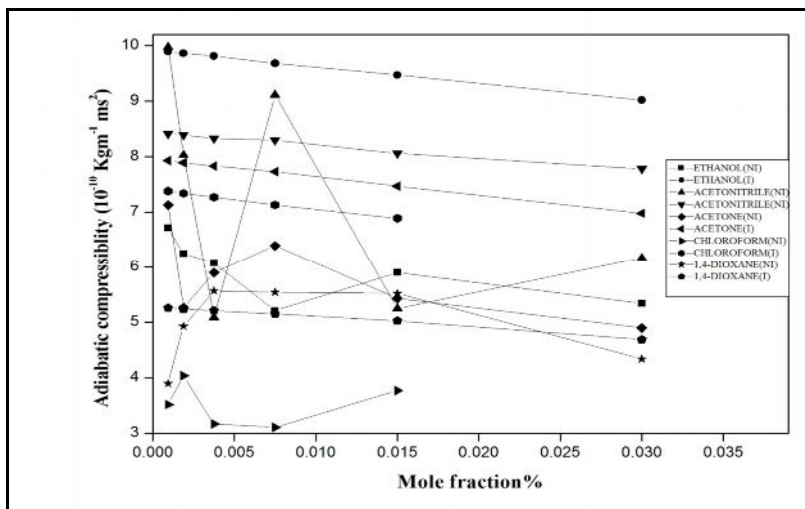


Fig. 3 Adiabatic compressibility ($\text{Kg}^{-1} \text{ms}^2$) Vs Mole fraction% graph for 2'chloro-4methoxy-3nitro benzilic acid in different solvents (shown in the inset)

The decrease in adiabatic compressibility with further increase in concentration indicates the breakdown of the network formed by the solvent molecules. . A monotonous decreasing nature of adiabatic compressibility (as well as inter molecular free length) is observed with increase in the mole fraction of polar solvents which assures that the systems shows structural compactness. Compressibility is the measure of the ease with which a system can easily be compressed. i.e., the larger the compressibility the easier it can be compressed because of more frees space between the components [16]. Adiabatic compressibility reaches a minimum at 0.0075 mol% beyond this concentration there is an increase in the adiabatic compressibility with an increase in concentration. This indicates that the solute/solvent interaction is replaced by comparatively stronger interaction between solute molecules, releasing the solvent molecules. Further increase in adiabatic compressibility indicates a change in the conformation /orientation of the solute molecules in solution, leading to weaker Inter-molecular interaction. This is attributed to the steric requirement of arranging an increasing number of larger molecules. In this situation, the steric factor takes predominance over intermolecular interactions. An increase in adiabatic compressibility indicates a change in the arrangement of the solvent molecules around the solute molecule undergoing conformational change, which results in weakening of the

solute/solvent interactions. This means that the solution becomes more compressible. It also indicates the associating tendency of the solute molecules in solution.

The decrease of intermolecular free length with increase in concentration is a normal trend [17]. The free length is the distance between the surfaces of the neighbouring molecules. It indicates significant interactions between the solute and solvent molecules, due to which the structural arrangement in the neighbourhood of constituent solute particles is considerably affected.

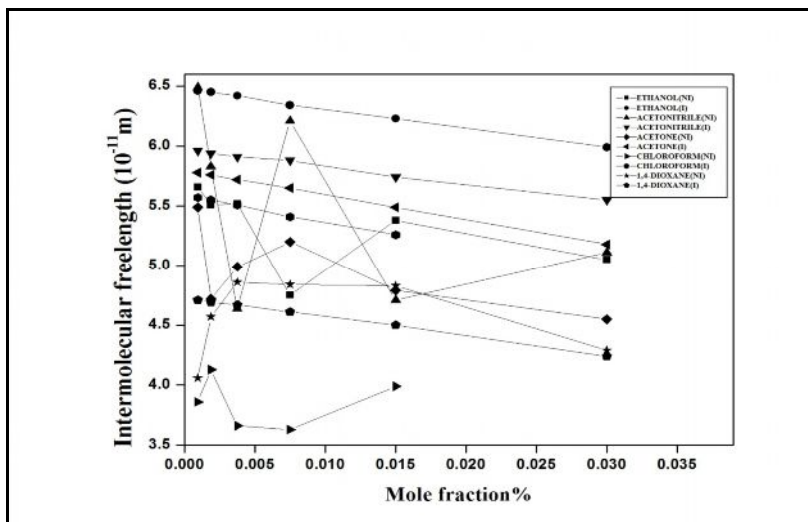


Fig. 4 Intermolecular free length (10^{-11} m) Vs Mole fraction% graph for 2'-chloro-4-methoxy-3-nitro benzilic acid in different solvents (shown in the inset)

At lower concentrations, the molecules are not closer and then the intermolecular free length will be high. As the concentration increases, the molecules come closer, thereby decreasing the intermolecular free length and hence internal pressure increases. Intermolecular free length and adiabatic compressibility are directly related to each other [18,19]. Hence, the adiabatic compressibility increases with an increase in intermolecular free length (Fig.4).

Therefore, intermolecular free length is one of the predominating factors for deciding the nature of variation in ultrasonic parameters in the liquid mixture. The intermolecular free length and ultrasonic velocity are inversely related to each other [14, 15]. The ultrasonic velocity increases with a decrease in the intermolecular free length. The initial increase of free length with an increase in molar concentration shows the reduction in the degree of association among solvent molecules. This is due to the loss of dipolar association; breaking up of hydrogen bonds and differences in the size and shapes of molecules in the liquid mixtures [20,21]. The formation of weaker intermolecular interaction leads to an increase in adiabatic compressibility and intermolecular free length. The stronger intermolecular interactions results in a tightly packed liquid structure, and, as such, the adiabatic compressibility and intermolecular free length decreases.

The relative association is the measure of extent of association of components in the medium. It is a property of understanding the molecular interaction in liquid mixtures and solutions. The relative association, R_A is influenced by two factors:

- i) breaking up of solvent/solvent interaction on addition of solute indicates higher value of R_A
- ii) Solvation of solute indicates a lower value of R_A

Relative association which shows the increasing trend also confirms the existence of molecular association between the different components of the mixture [22]. Relative association is found to have an initial minimum value at 0.001875 mole % for polar solvent (Fig.5). Beyond this concentration, the R_A values increase, reaching a maximum at 0.0075 mole %. The maxima and minima are shifted to low concentration regions of 0.0075mole% and 0.001875 mole%, respectively. Further, the addition of 2C4MBA does not affect the existing intermolecular interactions significantly. This trend can be explained that at low concentration, the solvent/solvent interactions break down to give way to solvent/solute interactions.

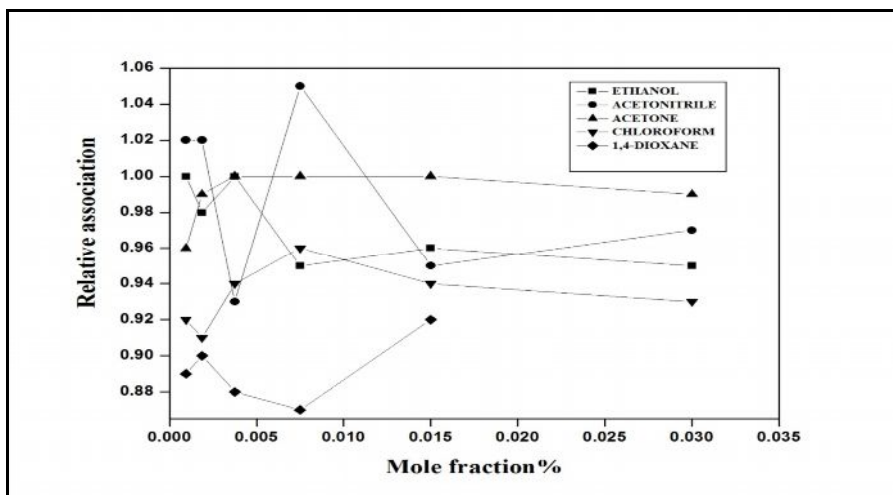


Fig. 5 Relative Association Vs Mole fraction% graph for 2'chloro-4methoxy-3nitro benzilic acid in different solvents (shown in the inset)

The decrease in free volume suggests the close packing of the molecules, which may be concluded as the increasing magnitude of the interaction [23-25]. In the concentration range of 0.0009-0.001875 mole%, there is a sharp decrease in apparent molar volume for polar solvent as the concentration increases. This clearly shows that within the concentration range a significant solute-solvent interaction is taking place. Beyond this concentration range, the decrease in molar volume is not very significant. For non polar solvent there is a sharp increase in apparent molar volume at 0.00375mole %. This is explained as increase in concentration allows for close approach of solvent and solute molecules and stronger association between solute and solvent molecules. This leads to decrease in volume and an increase in the density of the solution. The strength of interaction between component molecules is well reflected in deviations observed in K_s, ρ , U , and L_f from the expected trend. The excess parameters are found to be more sensitive towards intermolecular interactions in the binary mixture. An ideal solution should be considered as non-associated and for an ideal mixture the values of excess property is zero. For non-ideal mixtures, the difference between experimental values and ideal values is significant. Excess functions were calculated using the general formula [19].

For ideal binary mixtures:

$$Y^E = Y_{exp} - Y_{ideal} = 0 \quad (5)$$

$$Y_{ideal} = Y_{exp} \quad (6)$$

In general, for non-ideal mixtures

$$Y^E = Y_{exp} - Y_{ideal} \quad (7)$$

$$Y_{ideal} = [(1-x) Y_1 + xY_2] \quad (8)$$

Where x is mole fraction of 2C4MBA. Y^E is excess adiabatic compressibility or excess intermolecular frelength or excess velocity or excess density and subscripts 1 and 2 stand for ethanol, acetonitrile, chloroform, acetone, 1,4-dioxane and 2C4MBA, respectively.

For non ideal mixtures, depending upon the magnitude and type of intermolecular interactions or changes in concentration and orientation of solute molecules in solution, the magnitude and the sign of excess values also change.

The excess parameters are a measure of deviation from ideal behavior and are found to be highly sensitive to intermolecular interactions between component molecules of the mixture. Weak interaction between unlike molecules gives positive excess values whereas those of dipole-dipole, dipole-induced dipole, charge transfer, and hydrogen bonding between unlike molecules gives negative excess parameters.

The negative values of some thermo-acoustic parameters like excess compressibility indicate a strong intermolecular interaction in the constituent molecules due to presence of hydroxyl group of binary liquid mixture and it may lead to the formation of weak complex in the liquid mixture at particular concentration. β_E values are negative which suggest the presence of hydrogen bonding interaction between the components of the liquid mixtures. However, β_E values are positive which suggest the absence of hydrogen bonding.

This results in the formation of a more compact structure due to hydrogen bonding between unlike molecules. The positive values of excess adiabatic compressibility, excess intermolecular free length, and negative excess velocity, indicate weaker interactions between solute and solvent molecules, resulting from the disruption of molecular association (Figs. 6, 7 and 8).

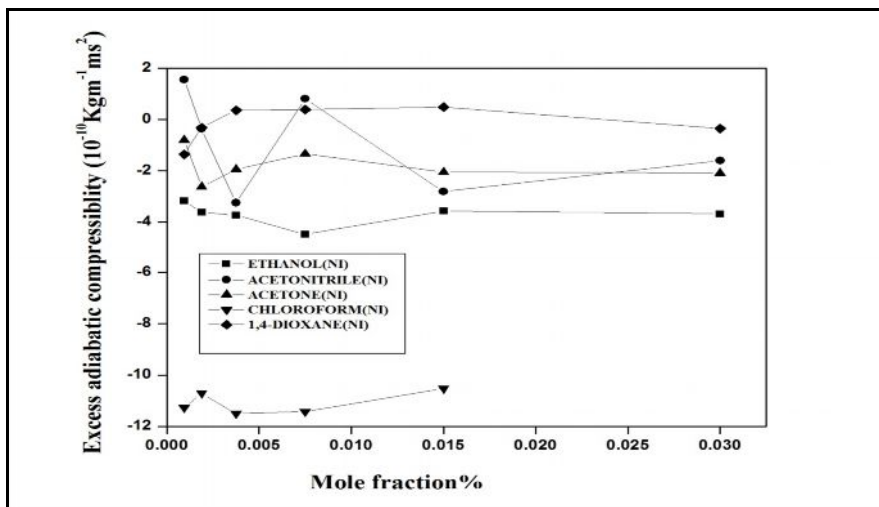


Fig.6: Excess adiabatic compressibility (Kg⁻¹ms²) Vs Mole fraction% graph for 2'chloro-4methoxy-3nitro benzoic acid in different solvents (shown in the inset)

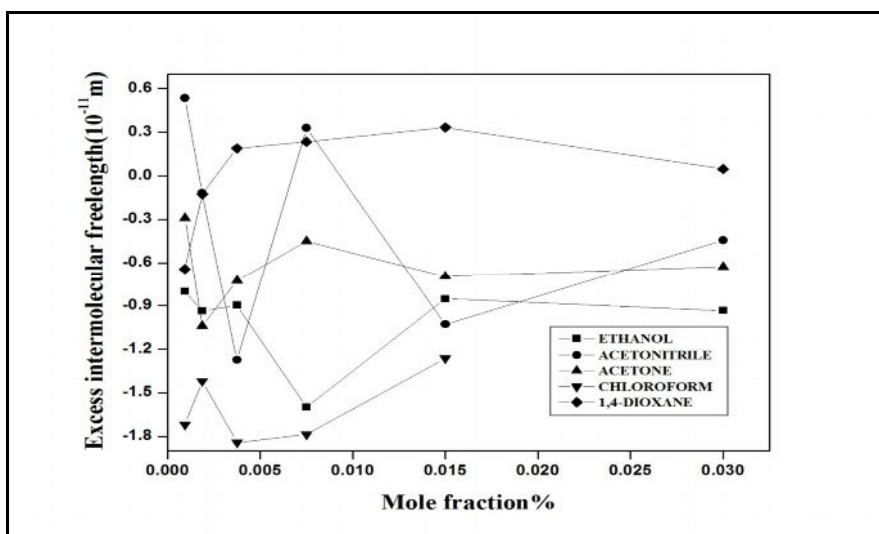


Fig. 7 Excess intermolecular frelength A⁰ Vs Mole fraction% graph for 2'chloro-4methoxy-3nitro benzoic acid in different solvents (shown in the inset)

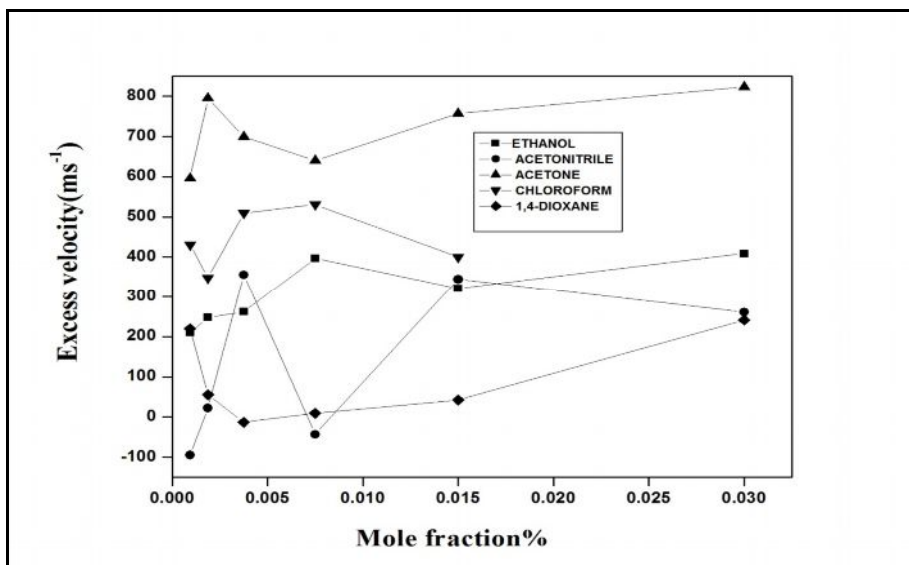


Fig. 8 Excess Velocity ms^{-1} Vs Mole fraction% graph for 2'chloro-4methoxy-3nitro benzoic acid in different solvents (shown in the inset)

The negative value of excess volumes shows that the existence of interactions between solute and solvent molecules is apparent. A positive excess acoustic impedance value indicates that over the concentration range of 0.000185 - 0.00375 mole% for polar solvents that significant interaction between solute and solvent is present. The negative excess adiabatic compressibility and excess intermolecular free length are attributed to the presence of intermolecular interaction between solute and solvent. This is especially true for solutions of concentration of mole fraction 0.0075-0.0015% for polar solvents and 0.000938 - 0.001875 mole% for non polar solvents. The rate of disruption of intermolecular interaction between solvent molecules is increased as the polarity of the solvent is increased. .

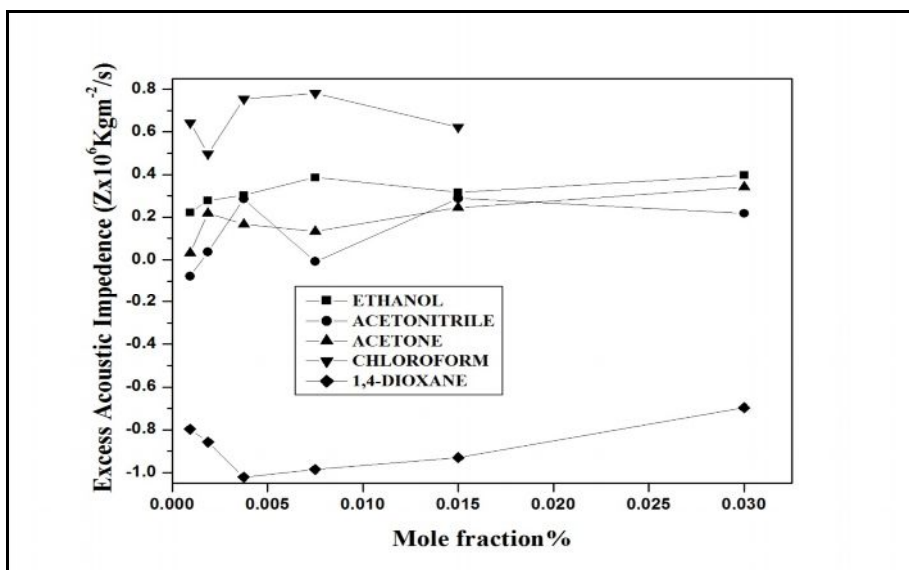


Fig.9 Excess Acoustic Impedance ($Z \times 10^6 \text{Kgm}^{-2}/\text{S}$) Vs Mole fraction% graph for 2'chloro-4methoxy-3nitro benzoic acid in different solvents (shown in the inset)

Thus, the positive excess velocity, acoustic impedance (Fig. 9) and negative excess K_s and L_f may be attributed to specific, strong interactions like hydrogen bonding and dipole-dipole interactions, while the negative deviations may be ascribed to weak dispersion forces in the system. Oswal and Desai [26, 27] attributed the positive excess K_s and L_f values to the large size of the solute molecules and weaker cohesive forces between unlike components of the solution, as in the present system.

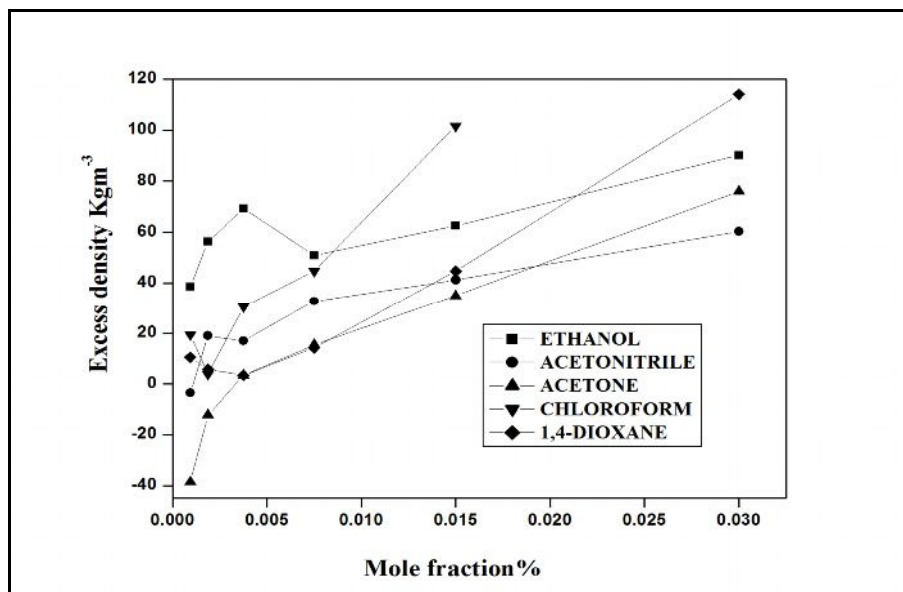


Figure .10 Excess Density (Kg/m³) Vs Mole fraction% graph for 2'chloro-4methoxy-3nitro benzilic acid in different solvents (shown in the inset)

In (Fig. 10) at a concentration of 0.03 mol% a maximum for excess density for polar solvents indicates that solvent–solvent interactions are replaced by solvent–solute interactions. The values of excess density in all the solvents at different mole fraction are found to be both positive and negative. The nature of sign changes when the mole fraction is increased in all solvents. This is due to the weakening of the molecular interaction between the molecules.

4. Conclusion

The ultrasonic velocity, density, adiabatic compressibility and other related parameters were calculated. Variation of acoustic parameters with concentration indicates the presence of specific interaction due to dipole-dipole interaction, dipole induced dipole and hydrogen bonding interactions between the solute and solvent. Polar solvent is capable of taking part in intermolecular hydrogen bonding interactions which are being slowly replaced by solvent-solute interaction. This leads to the solvation of the solute particles resulting in an increase in volume and a decrease in density of the mixture. In non-polar solvents, at higher concentration the dipole induced dipole interaction increases leading to decrease in volume. The excess parameters are a measure of deviation from ideal behavior and are found to be highly sensitive to intermolecular interactions between component molecules of the mixture. Weak interaction between unlike molecules gives positive excess values whereas those of dipole-dipole, dipole-induced dipole and hydrogen bonding between unlike molecules give negative excess parameters. This study concluded that the type and the magnitude of interaction depend on the polarity of the solvent and concentration of the solute.

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References

1. S Elangovan and S Mullainathan, Indian J. Phys. 2013,87, 373.
2. S Elangovan and S Mullainathan, Indian J. Phys. 2013, 87 ,659.
3. R N Shelar, R Y Borse and A B Sawant, Indian J. Phys. 2010, 84, 81.
4. Eyring, H.andkincaid, J.F, J.Chem, Phys, 1938, 6 ,620.
5. Singh, S.,Singh,R.,Prasad, N.and prakash.S., Ind.J.Pure and Appl.Phy., 1977, 3 ,156 .
6. Ramamurthy, M.and sastry, O.S., Indian. J.Pure and Appl. Phys., 1983, 21, 579.
7. Ramasamy.K.and Ranganathan.V., Indian J.Pure and Appl. Phys., 1970, 8, 144.
8. Negakuva., J.Am. Chem. Soc., 1954, 76, 3070 .

9. Hobbs, M.E. and Bates, W.W., J.Am. Chem. Soc., 1952, 74, 746.
10. Freedman, E., J.Chem. Phys., 1955, 21, 1784.
11. Kannappan, A.N. and Rajendran, V., Indian J.Pure and Appl. Phys., 1992, 30, 176.
12. Ali A, Hyder S and. Nain AK , Journal of Molecular liquids, 1999, 79 ,89-99.
13. A. Ali, A.K. Nain, Ind. J. Pure Appl. Phys.1997, 35, 729.
14. R.J. Fork, W.R. Moore, Trans Faraday Sco., 1965, 61, 2105 .
15. A. Ali, A.K. Nain, M. Kamil, Thermochem. Acta. 1996, 274, 209.
16. A. Ali, A.K. Nain, Acoust. Lett. 1996, 19, 181 .
17. Amalendu Pal, Sanjay Sharma and Arvind Kumar, Indian J.Pure Appl. Phys., 2000,38,174.
18. A. Ali, A.K. Nain, Ultrason 1999, 21, pp31-34.
19. A. Ali, A.K. Nain, M. Ibrahim, J.pure Appl.Ultrason. 1997, 19, 4.
20. A. Ali, S. Hyder, A.K. Nain, Indian.J.Phys. 2000, 74, B9 1063-67.
21. T. Sivaprasad, P. Venkateswarlu, Acoust. Lett. 1994,18, 1.
22. V.A. Tabhane, O.P. Chimankar, S. Manja, T.K.J. Nambinarayanan, Pure Appl.Ultrason. 1999, 21 ,67–70.
23. J Pal, Gurcharan Dass & Harsh Kumar, J.Pure and Appl.Ultrason, 2001, 23, 10.
24. T S Banipal & A F Toor & V K Rattan, Indian J Chem. 2000, 39A ,809.
25. P S Naidu & K Ravindra Prasad, Indian J.Pure and Appl. Phys., 2002, 40, 264.
26. G Arul & L Palaniappan, Indian J pure and Appl. Phys. 2001, 39, 561.
27. S.L. Oswal, Desaih, Fluid Phase Equilibra 1998, 149, 359.
28. A. Ali, A. Nain, Indian J. Pure Appl. Phys. 2001, 39 421–427
