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Research Paper

Ultrasonic and Molecular Interaction Studies of 2-Chlorobenzaldehyde with Iodine in Hexane at 303K

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Ultrasonic velocity, viscosity and density of 2-chlorobenzaldehyde with iodine in hexane ternary solution has been measured at 303K in different concentrations. Ultrasonic velocity has been measured using single frequency interferometer at 2 MHz (Model F-81). By using the Ultrasonic velocity(u), density(ρ) and coefficient of viscosity(η), the acoustical parameters like adiabatic compressibility(κ),free length (L_f), interaction parameter(α), Free volume(V_f) were calculated. The results have been used to discuss the nature and strength of intermolecular interactions. The results have been discussed in terms of solute-solute and solute-solvent interactions between the component and the compatibility of these methods in predicting the interactions in these mixtures has also been discussed.

Key Words: 2-Chlorobenzaldehyde; Iodine; Hexane; Ultrasonic Velocity; Molecular Interactions

Introduction

The studies on volumetric, ultrasonic and viscometric properties of liquid mixtures and their dependence on composition and temperature are of importance in many fields of applied research and find applications in many important chemical, textile, Leather, Industrial and Biological process. Ultrasonic velocity measurement have been successfully employed to detect and assess weak and strong molecular interactions, present in binary and ternary liquid mixtures [1, 2]. Ultrasonic studies have found wide applications owing to their ability to characterize the physico-chemical behaviour of solutions. The excess properties have been claimed to be an aid in the characterization of the molecular interactions that are present in solutions and liquid mixtures. This is achieved through elevation of ideal quantities. In recent years, considerable efforts have been given for the elevation of ideal and excess thermodynamic quantities of binary and ternary liquid mixtures [3, 4]. The study of molecular interaction in the liquid mixtures is of considerable in the elucidation of the structural properties of the molecules.

The nature and degree of molecular interactions in different solutions depend upon the nature of the medium, the structure of the solute molecule and also the extent of solvation taking place in solution. Since, acoustic parameters provide a better insight into molecular environment to liquid mixtures, it seemed important to study molecular interactions which motivated the authors to carry out the present investigation in the ternary liquid mixtures of 2-chlorobenzaldehyde with iodine in hexane using ultrasonic technique.

Materials and Methods

In the present paper, we report densities ρ and Ultrasonic velocities of ternary mixtures of 2-chlorobenzaldehyde with Iodine in Hexane at 303K, over the entire composition range. Iodine (AR-

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Ranbaxy fine chemicals limited) is used as such. The solvent has taken as accurately weighted amount of sample was dissolved in suitable solvent to obtain solution in the concentration range 1 x 10^{-3} M-1 x 10^{-2} M. The ultrasonic velocity (U) have been measured in ultrasonic interferometer (Model F81) supplied by Mittal enterprises, New Delhi operating at a frequency of 2MHZ with an accuracy of ±0.1%. The Viscosities (η) of pure compounds and their mixtures were determined using Oswald's Viscometer calibrated with double distilled water [6, 7]. The densities (ρ) of pure compounds and their solutions were measured accurately using 10 ml specific gravity bottles in an electronic balance precisely and the accuracy in weighing is ±0.1mg.

The temperatures were controlled by circulating water around the liquid cell from a thermostatically controlled water bath (accuracy ±0.1°C). The temperature of the cell was measured using a thermocouple (at the crystal) and was found to be accurate to ±0.25°C. Using the measured data of U, ρ, $\eta$and the acoustical parameters such as adiabatic compressibility (β), free length (L_f), absorption co-efficient (α/f^2), Free Volume (V_f) and internal Pressure (π_i) have been calculated [8, 9].

$$\beta = 1 / U^2 \rho \ Kg^{-1}ms^2 \quad (1)$$

$$\alpha/f^2 = 8\pi^2\eta / 3\rho U^3 \ Nps^2m^{-1} \quad (2)$$

$$L_f = K / \sqrt{U\rho} \ Å \quad (3)$$

where K - is a temperature dependent constant.

$$V_f = (M_{eff} U/K\eta)^{3/2} \ m^3 \ mol^{-1} \quad (4)$$

where, M_{eff} is the effective molecular weight which is expressed as ($M_{eff} = Sx_im_i$ in which m_i and xi are the molecular weight and the mole fraction of the individual constituents respectively.

The following equation (5) was used to compute internal pressure (π_i).

$$\pi_i = bRT \ (K\eta / U)^{1/2} \ (\rho^{2/3}/M_{eff}^{7/6}) \ atm \quad (5)$$

where b - is the cubic packing factor which is assumed to be two for all liquids and solutions, K- the temperature constant whose value is 4.28 x 10^9, R-gas constant.

Results and Discussion

In the present investigation, ultrasonic velocity measurement is used to assess molecular interaction between 2-chlorobenzaldehyde with iodine in hexane [10, 11]. The values of U, ρ and $\eta$of mixtures and other computed acoustical parameters are given in Tables 1 and 2. Plot of ultrasonic velocity *versus* concentration are shown in Fig. 1. It is evident from the values of that ultrasonic velocity decreases with increase in concentration suggesting increase in solvation with concentration. It is obvious that the ultrasonic velocity of mixture is always higher than that of 2-chlorobenzaldehyde or iodine and increases with increase in the concentration of donor or acceptor. This suggests that there is strong molecular interaction between the components [12, 13].

Density is a measure of solvent-solvent and ion-solvent interactions. Increase in density with concentration indicates the increase in solvent-solvent and solute-solute interactions; whereas density decreases in density indicates the lesser magnitude of solute-solvent and solvent-solvent interactions. Increase in density with concentration is due to shrinkage in the volume which in turn is due to presence of solute molecules. In other words, the increase in density may be interpreted to the structure-maker (or) the solvent due to added solute.

Similarly, the decrease in density with concentration indicates the structure-breaker of the solvent. It may also be true that solvent-solvent interactions bring about a bonding, probably hydrogen bonding between them. Usually, the values of density and viscosity of any system vary with increase in concentration of solutions [14, 15]. The change in structure of solvent or solutions as a result of hydrogen bond formation or dissociation or hydrophobic (structure-breaking) or hydrophilic (structure-forming) character of solute. That is hydrogen bond forming or dissociation properties can thus be correlated with change in density and viscosity. Viscosity is an important parameter in understanding the structure as well as molecular interactions occurring in the solutions. Viscosity variation is attributed to the structural changes. The structural changes influence the viscosity to a certain extent as compared to density

Table 1: The Experimental values of ultrasonic velocity, density, viscosity and the other acoustical parameters for Iodine +2-chlorobenzaldehyde in hexane system at 303K

CONC. (M)	Velocity (u) ms^{-1}	Density (ρ) kgm^{-3}	Viscosity (η) 10^{-3}	Compressibility (β) 10^{-10} kg^{-1} ms^2	Free length (L_f) 10^{-11}m	Molar volume (V_m)10^{-4} m^3	Available volume (V_a)$10^{-5}m^3$	L.J.P
0.001	1056.5	661.9	0.4840	13.54	7.358	1.302	4.424	4.663
0.002	1055.1	662.0	0.4831	13.57	7.367	1.303	4.436	4.618
0.003	1054.7	662.9	0.4838	13.56	7.365	1.301	4.435	4.605
0.004	1051.3	663.0	0.4934	13.65	7.388	1.302	4.464	4.496
0.005	1053.8	665.7	0.4895	13.53	7.356	1.297	4.427	4.576
0.006	1057.0	664.4	0.4913	13.47	7.341	1.300	4.411	4.680
0.007	1054.8	666.7	0.4943	13.48	7.343	1.296	4.415	4.608
0.008	1055.2	665.5	0.4971	13.50	7.347	1.298	4.421	4.621
0.009	1056.0	666.7	0.4921	13.45	7.335	1.297	4.408	4.647
0.010	1054.4	666.5	0.4883	13.50	7.347	1.297	4.424	4.595

Table 2: The Experimental values of the other acoustical parameters for Iodine +2-chlorobenzaldehyde in hexane system at 303K

CONC. (M)	Internal pressure (π_i)10^8 atm	CE 10^4 $KJmol^{-1}$	Free volume (V_f)10^{-7} m^3	Relaxation time (τ) 10^{-13} S	delta G* 10^{-19} $KJmol^{-1}$	Impedance (Z) 10^5 ms^{-1} kgm^{-3}	Interaction parameter (α_i)
0.001	2.957	3.852	2.915	8.735	3.99722	6.993	–0.0354
0.002	2.956	3.850	2.919	8.740	3.99725	6.985	–0.0381
0.003	2.960	3.852	2.913	8.748	3.99729	6.992	–0.0390
0.004	2.993	3.896	2.816	8.978	3.99837	6.970	–0.0453
0.005	2.984	3.870	2.861	8.829	3.99767	7.015	–0.0409
0.006	2.980	3.874	2.860	8.825	3.99765	7.023	–0.0353
0.007	2.998	3.885	2.827	8.885	3.99794	7.032	–0.0394
0.008	3.001	3.897	2.806	8.945	3.99822	7.022	–0.0389
0.009	2.988	3.873	2.853	8.825	3.99766	7.040	–0.0376
0.010	2.976	3.862	2.881	8.786	3.99747	7.028	–0.0407

and compressibility. It is observed that the values of h increases with increase in solute concentration in the system. This increasing trend indicates the existence of molecular interaction occurring in this systems. Fig. 2 shows the plot of adiabatic compressibility *versus* concentration. b values can be used to ascertain the molecular interaction in solution. b values decreases with increase in concentration and increases. The reverse trends in k values with concentration to that of ultrasonic velocity support the existence of interactions between iodine and 2-chlorobenzaldehyde. Adiabatic compressibility,

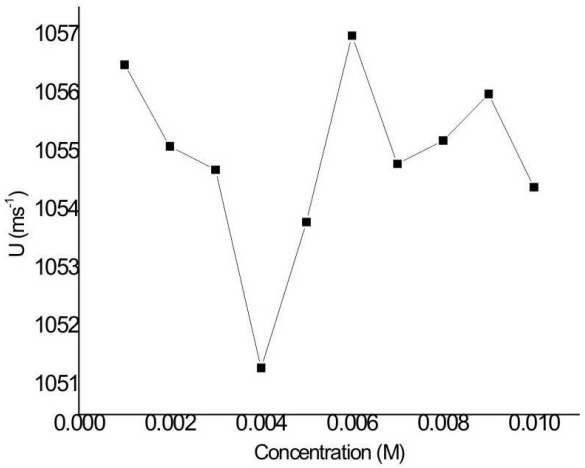

Fig. 1: Plot of Ultrasonic velocity *versus* equimolar concentration of 2chloro benzaldehyde and Iodine in hexane at 303K

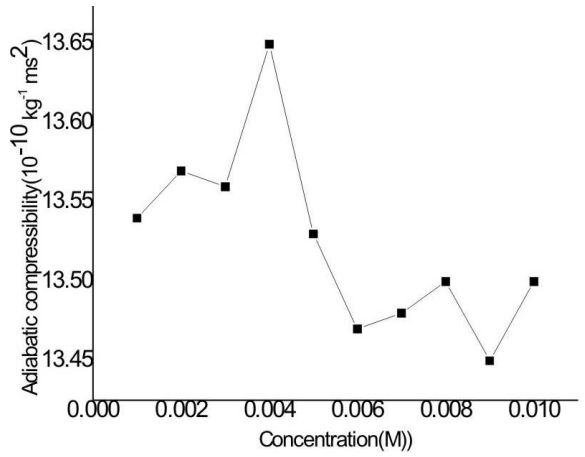

Fig. 2: Plot of adiabatic compressibility *versus* equimolar concentration of 2-chloro benzaldehyde and Iodine in hexane at 303K

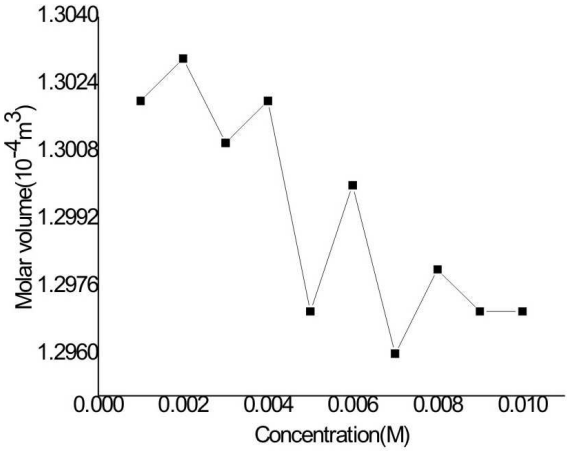

Fig. 3: Plot of Molar volume *versus* equi molar concentration of 2-chlorobenzaldehyde and iodine in hexane at 303K

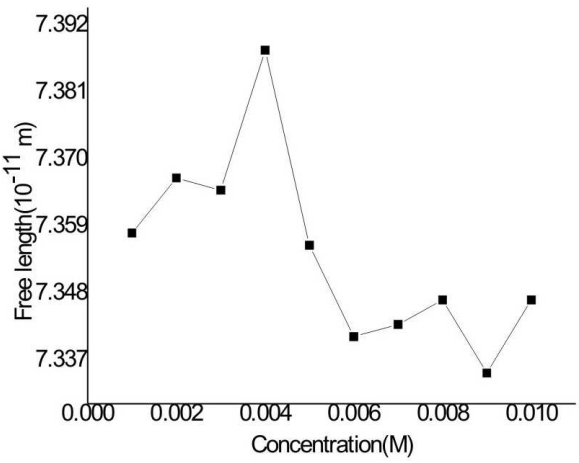

Fig. 4: Plot of free length *versus* equimolar concentration of 2-chlorobenzaldehyde and iodine in hexane solution at 303K

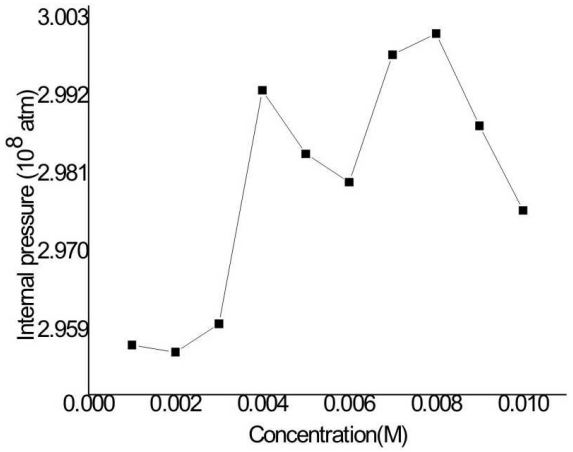

Fig. 5: Plot of internal pressure *versus* equimolar concentration of 2-chlorobenzaldehyde and iodine in hexane at 303K

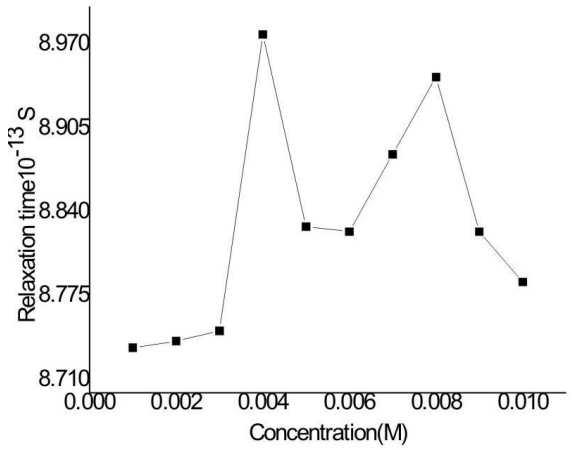

Fig. 6: Plot of relaxation time *versus* concentration equimolar concentration of 2-chlorobenzaldehyde and iodine in hexane at 303K

intermolecular free length and free volume are continuously decreases with increasing mole fraction whereas internal pressure is in increasing trend. A reduction in adiabatic compressibility is an indication that component molecules are held close to each other. Thus, addition of solvent makes all components to be closer. This idea is supported by the decreasing trend of intermolecular free length (Fig. 4). Free volume and internal pressure are behaving opposite to each other (Figs. 5 and 6). Free volume shows a decreasing trend with increasing mole fraction of hexane. The addition of hexane with a mixture leads to a compact structure due to presence of dipolar type interaction. This contributes to the decrease in free volume values and the internal pressure shows an increasing trend. The interaction parameter (c_i) are found to be negative which strongly confirm the presence of strong interactions between the unlike molecules.

Conclusion

In this work, the ultrasonic parameters of 2-chlorobenzaldehyde with iodine in hexane were measured. Authors have found out, the decrease in intermolecular free length indicates the interaction between the solute and solvent molecules due to which the structural arrangement in the neighbourhood of constituent ions (or) molecules gets affected considerably. These are slight decrease in the L_f value in the mixture especially when the concentration of donor and acceptor increase at 0.004M and decrease at 0.009M.

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