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Ultrasonic studies of salicilaldehyde with acetone in hexane at different temperatures

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ABSTRACT

The ternary mixture of salicilaldehyde with acetone in hexane has been studied extensively from the view point of their acoustic and molecular interaction studies at 293, 298, 303 and 308K. The variations in these parameters have been studied in terms of nature and extent of interaction. These properties have been used to calculate various thermo-chemical parameters. Experimental values are used to compute derived parameters. By using the Ultrasonic velocity (u), density (ρ) and coefficient of viscosity (η), the other acoustical parameters adiabatic compressibility (β), free length (L_f), interaction parameter (α), molar volume (V_m) were calculated. The study reveals that weak interaction takes place at higher temperatures of the ternary mixtures.

Key words: salicilaldehyde-Ultrasonic velocity- free length-molecular interactions

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INTRODUCTION

The study of molecular interactions plays an important role in understanding the structure and properties of liquids and gases**.** Ultrasonic velocity of a liquid is fundamentally related to the binding forces between the atoms or the molecules and has been adequately employed in understanding the nature of molecular interaction in pure liquids, binary and ternary mixture[1-3].The deviations from the linear dependence of velocity and compressibility provide an insight into the physio-chemical properties of liquid mixtures such as molecular association and dissociation as well as the strength of interaction between the components[4-5]. Variation in thermal and acoustic properties with temperature provides added information regarding the binary and ternary system. As a part of our ongoing research work, the present investigation deals with three important liquids namely salicilaldehyde with acetone in hexane at 293,298,303 and 308K over the entire range of concentrations. The liquid under investigation are very useful chemicals and of industrial significance. The variation of ultrasonic velocity and related parameters throw much light upon the structural changes associated with the liquid mixtures having weakly interacting components as well as strongly interacting components[6-7].

EXPERIMENTAL SECTION

Materials and methods

Liquid mixtures of various concentrations in mole fraction are prepared by taking AR grade chemicals, which are purified by standard methods[8-9]**.** In the present work, the densities (ρ) and ultrasonic velocities (U) of ternary

mixtures of salicilaldehyde with acetone in hexane at 293, 298, 303 and 308K over the entire composition range are measured at different concentrations.

Experimental procedure

The solvent has taken as accurately weighted amount of sample was dissolved in suitable solvent to obtain solution in the concentration range between 0.001M to 0.10M. 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%. An Ostwald's viscometer (10 ml capacity) is used for the viscosity measurements. The temperature of the cell was measured using a thermocouple (at the crystal) and was found to be accurate, to ±0.25°C.

Theory and calculation

Using the measured data of sound velocity (U), density (ρ) and viscosity (η), the acoustical parameters such as adiabatic compressibility (κ), free length (L_f), free Volume (V_f) and internal pressure (π_i) have been calculated using the standard relations.

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

$$L_f = K/\sqrt{U\rho}\ Å \quad (2)$$

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

Where K- is the temperature dependent constant. M_{eff} is the effective molecular weight which is expressed as ($M_{eff} = \Sigma x_i m_i$ in which m_i and x_i are the molecular weight and the mole fraction of the individual constituents respectively).

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

$$\pi_i = bRT\ (K\eta/U)^{1/2}\ (\rho^{2/3}/M_{eff}^{7/6})\ atm \quad (4)$$

where b is the cubic packing factor which is assumed to be two for all liquids and solutions, K is the temperature constant whose value is $4.28x10^9$, R is the gas constant. The type of interaction present can be detected by ultrasonic velocity, density and viscosity measurements for different concentrations at 293,298, 303 and 308K.

RESULTS AND DISCUSSION

The experimental values of ultrasonic velocity **,**density, viscosity, adiabatic compressibility, free length, free volume, internal pressure and molar Volume of salicilaldehyde with acetone in hexane have been measured at 293,298,303 and 308K are listed in Table 1. The values of impedance, relaxation time and interaction parameter have been calculated and presented in Table 2. The variation of ultrasonic velocity (U) with equimolar concentration of solutes is shown in Fig. 1.The values of ultrasonic velocity decreases with increase in temperature. The variation of ultrasonic velocity depends upon the increase or decrease of intermolecular free length after mixing the components. Based on the model for sound propagation proposed by Eyring and kincaird, ultrasonic velocity (U) should increase, if the intermolecular free length (L_f) decreases and vice versa. This fact was noticed in the present study of the system. Table 1 shows the non linear variations of ultrasonic velocity with increase in concentration of the solute. It is known that such an increase in the close packed structure results in increased interaction between the molecules. The compressibility increases due to structural changes of molecules in the mixture leading to a decrease in ultrasonic velocity at higher temperature[10]. The adiabatic compressibility(κ) increases with increase in concentration at higher temperature, which suggests that intermolecular attraction persists even at higher temperature as shown in Fig. 2. The reverse trends in (κ) values with concentration to that of ultrasonic velocity support the existence of interactions between the components. The density (ρ) and viscosity (η) decreases with increase in concentration of the solute. The pronounced increase or decrease in these parameters with composition of mixtures indicates the presence of interactions between the components of molecules in the ternary mixtures. The value of velocity depends on the increase or decrease of intermolecular free length after mixing the components. Increase in density (ρ) with concentration is due to shrinkage in the volume which in turn 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[11,12]. The changes in the structure of solvent or solution may be formed as a result of hydrogen bond formation or dissociation character. It can be correlated with change in density and viscosity[13]. The values of viscosity provides some reliable information in the study of molecular interaction

Table 1-Experimental values of ρ,η, and U of salicilaldehyde with acetone in hexane solutions at 293K, 298K, 303K and 308K

Conc. (M)	**Density (ρ) (Kgm^{-3})**				**Viscosity(η) ($10^{-3}Nsm^{-2}$)**				**Velocity(U) (ms^{-1})**			
	293K	298K	303K	308K	293K	298K	303K	308K	293K	298K	303K	308K
0.001	665.2	663.3	662.4	659.5	0.5059	0.5054	0.5075	0.4791	1101.5	1067.0	1060.1	1041.0
0.002	665.5	664.0	662.5	659.2	0.5008	0.5047	0.5106	0.4798	1102.1	1066.5	1063.7	1044.8
0.003	664.6	664.6	662.0	659.3	0.5029	0.4968	0.5019	0.4839	1099.6	1065.4	1067.0	1041.2
0.004	666.0	663.3	660.8	659.4	0.5024	0.4992	0.5013	0.4846	1101.6	1064.3	1063.9	1043.7
0.005	664.4	664.4	661.0	658.5	0.4963	0.4990	0.5011	0.4873	1102.7	1063.4	1063.9	1041.8
0.006	664.5	663.5	660.5	659.2	0.4989	0.4999	0.5001	0.4881	1104.9	1065.6	1064.3	1038.5
0.007	664.8	664.8	660.7	659.3	0.4947	0.4985	0.5022	0.4852	1107.0	1065.9	1064.8	1039.0
0.008	664.9	664.5	660.9	659.9	0.5523	0.4976	0.5027	0.4951	1102.2	1061.4	1062.5	1036.4
0.009	664.3	663.6	660.4	659.1	0.5036	0.4976	0.5013	0.4905	1107.3	1064.1	1063.5	1036.5
0.010	664.1	663.5	661.4	660.3	0.5025	0.5015	0.5012	0.4868	1106.5	1064.4	1064.7	1039.8
	Adiabatic compressibility(κ) 10^{-10} $Kg^{-1}ms^2$				**Free length (L_f)10^{-10}m**				**Free Volume(V_f) 10^{-7} m^3 mol^{-1}**			
0.001	12.390	13.243	13.433	13.992	0.7040	0.7278	0.7330	0.7481	2.903	2.772	2.728	2.894
0.002	12.371	13.241	13.341	13.897	0.7035	0.7277	0.7305	0.7456	2.949	2.776	2.717	2.903
0.003	12.444	13.256	13.268	13.991	0.7055	0.7282	0.7285	0.7481	2.921	2.838	2.801	2.852
0.004	12.373	13.310	13.370	13.922	0.7035	0.7296	0.7313	0.7462	2.933	2.813	2.794	2.856
0.005	12.378	13.310	13.366	13.992	0.7037	0.7297	0.7312	0.7481	2.993	2.811	2.795	2.825
0.006	12.327	13.273	13.366	14.066	0.7022	0.7286	0.7312	0.7501	2.977	2.812	2.805	2.804
0.007	12.275	13.240	13.349	14.050	0.7007	0.7277	0.7307	0.7497	3.024	2.826	2.790	2.832
0.008	12.380	13.358	13.403	14.108	0.7037	0.7310	0.7322	0.7512	2.547	2.815	2.776	2.737
0.009	12.277	13.308	13.388	14.122	0.7008	0.7296	0.7318	0.7516	2.946	2.826	2.792	2.776
0.010	12.299	13.303	13.338	14.007	0.7014	0.7295	0.7304	0.7485	2.952	2.794	2.798	2.821
	Internal pressure (π_i)/ 10^8 atm				**Molar Volume(V_m) 10^{-4} m^3 mol^{-1}**				**Available volume(V_a) 10^{-5} m^3 mol^{-1}**			
0.001	2.874	2.962	3.026	3.007	1.2956	1.2993	1.3010	1.3067	4.036	4.036	4.390	4.566
0.002	2.859	2.963	3.030	3.003	1.2950	1.2979	1.3008	1.3074	4.030	4.030	4.360	4.537
0.003	2.866	2.943	2.998	3.021	1.2967	1.2968	1.3018	1.3072	4.056	4.056	4.337	4.565
0.004	2.866	2.948	2.997	3.019	1.2940	1.2993	1.3042	1.3069	4.031	4.031	4.370	4.544
0.005	2.842	2.952	2.996	3.028	1.2972	1.2972	1.3038	1.3088	4.032	4.032	4.369	4.566
0.006	2.847	2.949	2.992	3.037	1.2970	1.2989	1.3048	1.3074	4.013	4.013	4.369	4.588
0.007	2.833	2.948	2.997	3.028	1.2964	1.2964	1.3045	1.3073	3.995	3.995	4.363	4.584
0.008	3.000	2.951	3.003	3.064	1.2963	1.2970	1.3041	1.3061	4.033	4.033	4.381	4.601
0.009	2.857	2.944	2.996	3.047	1.2974	1.2988	1.3051	1.3077	3.995	3.995	4.376	4.605
0.010	2.854	2.955	2.997	3.035	1.2978	1.2990	1.3032	1.3053	4.003	4.003	4.360	4.570

Table 2 .Derived parameters of salicilaldehyde with acetone in hexane solutions at 293K, 298K, 303K and 308K

Conc. (M)	**Impedance(Z)$10^5$$Kg^{-1}$ m^2 s^{-1}**				**Relaxation time(ζ) 10^{-13}S**				**Lenord Jones Potential (LJP)**			
	293K	298K	303K	308K	293K	298K	303K	308K	293K	298K	303K	308K
0.001	7.327	7.077	7.022	6.865	8.357	8.924	9.089	8.939	6.258	5.010	4.781	4.174
0.002	7.334	7.082	7.047	6.887	8.261	8.909	9.082	8.891	6.281	4.994	4.900	4.291
0.003	7.308	7.081	7.064	6.865	8.345	8.780	8.879	9.027	6.185	4.957	5.011	4.180
0.004	7.337	7.060	7.030	6.882	8.289	8.858	8.936	8.995	6.262	4.920	4.907	4.257
0.005	7.326	7.065	7.032	6.860	8.191	8.856	8.931	9.091	6.304	4.890	4.907	4.198
0.006	7.342	7.070	7.030	6.846	8.202	8.847	8.913	9.154	6.390	4.964	4.920	4.097
0.007	7.359	7.086	7.035	6.850	8.097	8.799	8.938	9.089	6.473	4.974	4.937	4.112
0.008	7.329	7.053	7.022	6.839	9.117	8.863	8.984	9.313	6.285	4.824	4.860	4.033
0.009	7.356	7.061	7.023	6.832	8.244	8.829	8.948	9.236	6.484	4.914	4.894	4.036
0.010	7.348	7.062	7.042	6.866	8.241	8.895	8.914	9.092	6.453	4.924	4.934	4.137

Table 3 .Derived parameters of salicilaldehyde with acetone in hexane solutions at 293K, 298K, 303K and 308K

Conc. (M)	Cohesive Energy(CE) 10^4 KJ/Mol				Free energy of activation (ΔG^*) 10^{-19}KJ mol^{-1}			
	293K	298K	303K	308K	293K	298K	303K	308K
0.001	3.723	3.849	3.936	3.929	3.864	3.932	3.998	4.063
0.002	3.703	3.846	3.942	3.926	3.864	3.932	3.998	4.063
0.003	3.716	3.817	3.903	3.949	3.864	3.932	3.998	4.064
0.004	3.709	3.830	3.908	3.947	3.864	3.932	3.998	4.063
0.005	3.687	3.829	3.907	3.963	3.864	3.932	3.998	4.064
0.006	3.693	3.830	3.904	3.971	3.864	3.932	3.998	4.064
0.007	3.674	3.822	3.910	3.958	3.864	3.932	3.998	4.064
0.008	3.889	3.827	3.916	4.002	3.868	3.932	3.998	4.065
0.009	3.707	3.824	3.909	3.985	3.864	3.932	3.998	4.065
0.010	3.704	3.838	3.905	3.961	3.864	3.932	3.998	4.064

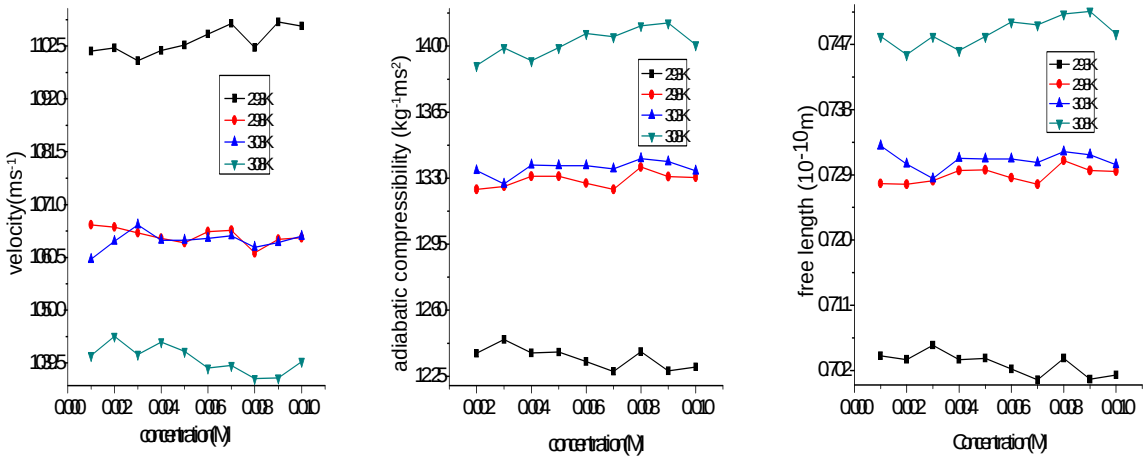

Table-2 shows that the viscosity increases with increase in concentration of the third component. From the Table 1, it is observed that the values of η decreases with increases in concentration. It indicates that the existence of molecular interaction. The free length(L_f) is almost constant in the concentration range investigated and this may be an intrinsic property of the complex. It indicates the small inter ionic distance. It further decreased with the increase in concentration due to the increasing the number of ions in a given volume or due to increase in compressibility. The additions of interacting molecules break up the molecular clustering of the other, releasing several dipoles for interaction. According to Eyring and Kincaid[14**],** intermolecular free length (L_f) is a predominant factor in salvation chemistry[15] and inversely related to ultrasonic velocity. The value of (L_f) is maximum at 0.008M at higher temperatures as sown in Fig. 3. The molar volume (V_m) and available volume(Va) increases with increase in concentration for the all temperatures. Moreover, molar volume (V_m) is also increases with rise in temperature in the present study which may probably would be caused from the fact that thermal energy facilitates an increase in the molecular separation[16] in the liquid mixtures which leads to an increase in molar volume (V_m) with elevation of temperature. The internal pressure (π_i) is the resultant of force of attraction and force of repulsion per unit area between the components as the internal pressure (π_i). The internal pressure(π_i) it may reflect the cohesive/adhesive forces available in the medium. The variation of the internal pressure may give some information regarding the nature and strength of the forces existing between the molecules. Internal pressure (π_i) increases when temperature increases.

The acoustical impedance (Z) is another parameter, is the product of velocity and density of mixtures. When an acoustic wave travels in a medium, there is a variation of pressure from particle to particle. The ratio of the instantaneous pressure excess at any particle of the medium to the instantaneous velocity of that particle is known as 'specific acoustic impedance' of the medium. The values of acoustic impedance (Z) is increases with the increasing of concentration. The increasing value of acoustic impedance supports the possibility of molecular interactions between unlike molecules. This factor is governed by the inertial and elastic properties of the medium. It is

important to examine specific acoustic impedance in relation to concentration and temperature. When a plane ultrasonic wave is set up in a liquid, the pressure and hence density and refractive index show specific variations with distance from the source along the direction of propagation. In the present investigation, it is observed that these acoustic impedance (Z) values increase with increasing concentration of salicilaldehyde. The values of cohesive energy(CE) and free energy of activation(ΔG^*) have been calculated and presented in Table 3. The cohesive energy (CE) decreases with the increase in concentration. The free energy of activation (ΔG^*) and relaxation time (τ) are intrinsic properties of a charge transfer complex. Free energy of activation (ΔG^*) is almost constant at different concentrations and the values are listed in Table 2. But, it is increases with the rise of temperatures. These two properties are almost constant. The relaxation time (τ) shows the increasing trend. The relaxation time depends upon the size and shape of the rotating molecular entities in the solution.

CONCLUSION

As hexane is weakly polar molecule, interactions are possible between salicilaldehyde and acetone. From the above observation, it may be concluded that intermolecular interaction takes place in the ternary system. The value of increase in free length (L_f) with increase in the concentration of solute at the temperature of 303.15K and 308.15K indicates that there is a weak solute-solvent interaction. The increase in intermolecular free length at 0.008M indicates the weak interaction between the solute and solvent molecules due to which the structural arrangement in the neighborhood of constituent ions (or) molecules gets affected considerably.

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