



Ultrasonic Investigation of Ternary Mixtures of Crotonaldehyde at 298.15, 303.15 and 308.15 K

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Densities, absolute viscosities and ultrasonic velocities of ternary mixtures of crotonaldehyde and acetone in hexane have been measured for the ternary mixtures at 298.15, 303.15 and 308.15 K in different concentrations under atmospheric pressure. These properties have been used to calculate various thermo-chemical parameters. The variations in these parameters have been studied in terms of nature and extent of interaction. By using the ultrasonic velocity (U), density (ρ) and coefficient of viscosity (η), other acoustical parameters were calculated. The non-linearity in the variation of viscosity is explained in terms of hydrogen bond formation between components of mixtures. The variation in ultrasonic velocity depends on the intermolecular free length on mixing. The value of intermolecular free length increases with increase in temperature and it is maximum at 308.15 K. It shows that weak interaction takes place at higher temperature. The results have been interpreted in terms of specific intermolecular interactions present in the mixtures and are found to support each other.

Keywords: Density, Adiabatic compressibility, Molar volume, Internal pressure.

INTRODUCTION

Carbonyl compounds contain polar group in which electron deficient carbon can function as electrophile. The experimental values of ultrasonic velocities along with densities are used to calculate the values of acoustical parameters such as adiabatic compressibility (κ), free length (L_f), internal pressure (π_i), molar volume (V_m) and available volume (V_a)¹⁻². The variation of these parameters with different concentrations is used to interpret the intermolecular interactions present among the liquid components. Thus data on some of the properties associated with the liquids and liquid mixtures like density and viscosity find extensive application in solution theory and molecular dynamics³. Intermolecular interaction studies as functions of concentration scale are useful in giving insight into the structure and bonding of associated molecular complex and other molecular processes⁴.

EXPERIMENTAL

Liquid mixtures of various concentrations in mole fraction are prepared by taking AR grade chemicals, which are purified by standard methods⁵. In the present work, the densities (ρ) and ultrasonic velocities (U) of ternary mixtures of crotonaldehyde with acetone in hexane at 298.15, 303.15 and 308.15 K

over the entire composition range are measured at different concentrations.

Experimental procedure: In this liquid system, the mole fraction of the first and second component was kept as equimolar concentration in the range between $1 \times 10^{-2}M$ to $1 \times 10^{-3}M$. The ultrasonic velocity in ternary mixtures have been measured using an ultrasonic interferometer (Mittal type-Model: F81) working at a frequency of 2 MHz with an overall accuracy of $\pm 2 \text{ ms}^{-1}$. The density and viscosity are measured using a specific gravity bottle and an Ostwald's viscometer with an accuracy of $\pm 0.1 \text{ mg}$ and $\pm 0.001 \text{ Nsm}^{-2}$, respectively. All the precautions were taken to minimize the possible experimental errors. The temperature is controlled by circulating water around the liquid cell from a thermostatically controlled water bath (accuracy $\pm 0.1 \text{ }^\circ\text{C}$).

Calculation of the derived parameters: Using the measured data of U , ρ and 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.

$$\kappa = 1/(U^2 \rho) \text{ (Kg}^{-1} \text{ m s}^2) \quad \dots (1)$$

$$L_f = K/\sqrt{U\rho} \text{ (\AA)} \quad \dots (2)$$

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

where, K - is the temperature dependent constant. M_{eff} is the effective molecular weight which is expressed as ($M_{\text{eff}} = \sum x_i m_i$)

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).

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

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 4.28×10^9 , R is the gas constant. The type of interaction present can be detected by ultrasonic velocity, density and viscosity measurements for different concentrations at 298.15, 303.15 and 308.15 K.

RESULTS AND DISCUSSION

The ultrasonic velocity (U), density (ρ), viscosity (η), adiabatic compressibility (κ), free length (L_f), free volume (V_f), internal pressure (π_i) and molar volume (V_m) of crotonaldehyde with acetone in hexane have been measured at 298.15, 303.15 and 308.15 K are presented in Table-1. The values of impedance, relaxation time, interaction parameter, cohesive energy and free energy of activation have been calculated and presented in Table-2. The density and viscosity 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. The variation of ultrasonic velocity (U) with equimolar concentration of solutes is shown in Fig. 1. Table-1 shows the increasing value 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 value of ultrasonic velocity (U) shows an inverse behavior as compared to the adiabatic compressibility (κ). Viscosity (η) is an important parameter used to study about the structure as well as molecular interactions occurring in the solutions. Due to structural changes, the value of viscosity may change. Density (ρ) is a measure of solvent-solvent and ion-solvent interactions. The increase of density with concentration indicates the increase in solvent-solvent and solute-solute interactions. The decrease in density indicates less magnitude of solute-solvent and solvent-solvent interactions. The values of density and viscosity of any system may vary with respect to the increase in concentration of solutions. The pronounced increase or

decrease in these parameters with various compositions of ternary mixtures indicates the presence of interactions between the components of molecules in the ternary mixtures. 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 viscosity⁶.

The calculated values of free length (L_f) for all the concentrations and three different temperatures are presented in Table-2. Free length is the distance between the surfaces of the neighboring molecules. The value of free length increases when the ultrasonic velocity increases at 298.15 K and 303.15 K. At 308.15 K, free length decreases. Intermolecular free length (L_f) denotes the magnitude of either the ion-ion interaction or the ion-solvent interaction or both. According to Eyring and Kincaid⁷, intermolecular free length (L_f) is a predominant factor in solvation chemistry⁸ and inversely related to ultrasonic velocity. Fig. 2 shows the variation of free length (L_f). In the present study, the intermolecular free length is found to decrease with increase in concentration and then increases indicating significant molecular interactions. Molar volume (V_m) shows an increasing trend with increase in concentration. Table-1 shows the values of available volume (V_a) with increase in concentration. Free volume (V_f) is the average velocity in which the center of the molecules can move inside the hypothetical cell due to the repulsion of surrounding molecules. Table-1 shows an increase in the free volume which is due to the loose packing of molecules.

Internal pressure is a measure of the change in the internal energy of liquid (or) liquid mixture, as it undergoes a very small isothermal change. Generally, 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 increases⁹. When the sound wave travels through a solution certain part of it travels through the medium and the rest gets reflected by the ion *i.e.*, restriction for the free flow of sound velocity by its ions. The character that determines this restriction or backward movement of sound waves is known as acoustic impedance (Z). It is important to examine specific acoustic impedance in relation to concentration and temperature. The increasing value of acoustic impedance supports the possibility of molecular interactions between unlike molecules.

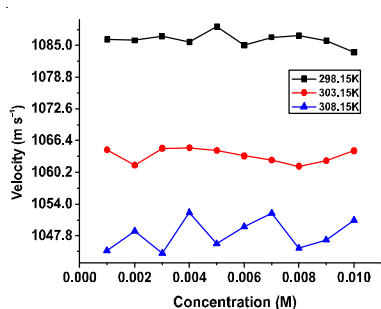


Fig. 1. Plot of ultrasonic velocity versus concentration of crotonaldehyde and acetone in *n*-hexane at different temperatures

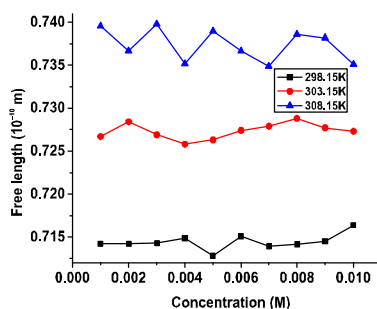


Fig. 2. Plot of free length versus concentration of crotonaldehyde and acetone in *n*-hexane at different temperatures

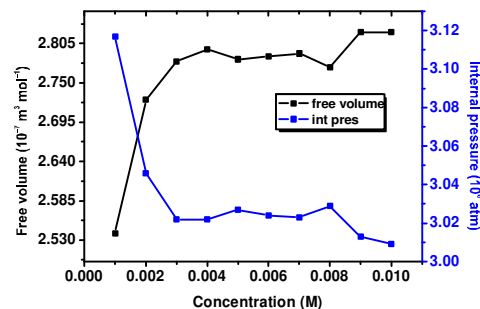
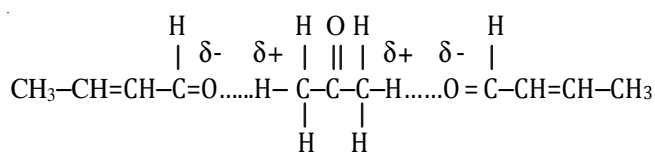


Fig. 3. Plot between internal pressure versus free volume of crotonaldehyde and acetone in *n*-hexane at 303.15 K

TABLE-1
EXPERIMENTAL VALUES OF ρ , η AND U OF CROTONALDEHYDE
WITH ACETONE IN HEXANE SOLUTIONS AT 298.15, 303.15 AND 308.15 K

Conc. (M)	Density (ρ) Kg m^{-3}			Viscosity (η) 10^{-3} Nsm $^{-2}$			Velocity (U) ms $^{-1}$		
	298.15 K	303.15 K	308.15 K	298.15 K	303.15 K	308.15 K	298.15 K	303.15 K	308.15 K
0.001	664.7	668.4	669.8	0.5120	0.5344	0.4932	1086.2	1064.6	1044.8
0.002	665.0	668.9	670.1	0.5160	0.5084	0.5049	1086.0	1061.6	1048.7
0.003	663.7	667.5	670.0	0.5162	0.5032	0.5033	1086.8	1064.9	1044.4
0.004	663.9	669.5	668.3	0.5157	0.5014	0.4949	1085.7	1065.0	1052.3
0.005	664.2	669.2	669.2	0.5116	0.5027	0.5018	1088.7	1064.5	1046.2
0.006	664.3	668.6	669.0	0.4907	0.5016	0.4970	1085.1	1063.4	1049.6
0.007	664.7	668.7	668.9	0.4984	0.5008	0.4941	1086.6	1062.6	1052.2
0.008	664.0	668.4	671.0	0.4991	0.5024	0.5056	1086.9	1061.4	1045.3
0.009	664.4	669.1	669.6	0.5013	0.4970	0.4993	1085.9	1062.5	1047.0
0.010	663.6	667.5	670.3	0.4970	0.4980	0.5144	1083.7	1064.4	1050.8
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 $^{-1}$					
	298.15 K	303.15 K	308.15 K	298.15 K	303.15 K	308.15 K	298.15 K	303.15 K	308.15 K
0.001	12.751	13.201	13.677	0.7142	0.7267	0.7396	2.792	2.540	2.786
0.002	12.751	13.265	13.569	0.7142	0.7284	0.7367	2.758	2.726	2.704
0.003	12.756	13.211	13.683	0.7143	0.7269	0.7398	2.760	2.780	2.700
0.004	12.779	13.170	13.513	0.7149	0.7258	0.7352	2.760	2.797	2.801
0.005	12.702	13.187	13.653	0.7128	0.7263	0.7390	2.803	2.783	2.720
0.006	12.785	13.226	13.568	0.7151	0.7274	0.7367	2.970	2.787	2.772
0.007	12.742	13.244	13.503	0.7139	0.7279	0.7349	2.907	2.791	2.806
0.008	12.749	13.280	13.639	0.7141	0.7288	0.7386	2.901	2.772	2.684
0.009	12.764	13.239	13.624	0.7145	0.7277	0.7382	2.878	2.821	2.741
0.010	12.832	13.223	13.511	0.7164	0.7273	0.7351	2.907	2.821	2.635
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 $^{-1}$					
	298.15 K	303.15 K	308.15 K	298.15 K	303.15 K	308.15 K	298.15 K	303.15 K	308.15 K
0.001	2.960	3.117	3.077	1.2964	1.2893	1.2866	4.163	4.314	4.464
0.002	2.973	3.046	3.109	1.2958	1.2882	1.2859	4.163	4.335	4.431
0.003	2.969	3.022	3.110	1.2982	1.2908	1.2860	4.164	4.317	4.466
0.004	2.969	3.022	3.067	1.2981	1.2872	1.2895	4.173	4.304	4.414
0.005	2.955	3.027	3.101	1.2971	1.2874	1.2874	4.145	4.309	4.456
0.006	2.899	3.024	3.080	1.2968	1.2884	1.2877	4.173	4.321	4.430
0.007	2.921	3.023	3.068	1.2959	1.2882	1.2878	4.158	4.327	4.409
0.008	2.921	3.029	3.120	1.2972	1.2887	1.2837	4.160	4.338	4.450
0.009	2.930	3.013	3.094	1.2963	1.2872	1.2863	4.165	4.324	4.446
0.010	2.918	3.009	3.137	1.2978	1.2902	1.2848	4.188	4.319	4.410

Positive values of molecular interaction parameters for all concentrations at 298.15 K indicate the presence of strong attractive force between the components. When temperature rises to 303.15 and 308.15 K, the negative sign of the values of interaction parameter shows weak interaction between the unlike molecules. It may be noted that such values are due to the electronic perturbation of the individual molecules during mixing and therefore, it depends very much on the nature of interaction between the molecules. The trend in cohesive energy (CE) is similar to that of internal pressure (π_i). The free energy of activation (ΔG^*) and relaxation time (τ) are intrinsic properties of a charge transfer complex. The value of ΔG^* increases with rise in temperature. These two properties are almost constant in the three systems. 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. A perusal on the magnitude of Lenord Jones potential (LJP) indicates that it is in the range of hydrogen bonding type of interaction. Free energy of activation (ΔG^*) is almost constant at different concentrations and the values are listed in Table-2. Fig. 3 depicts the comparison between free volume (V_f) and the internal pressure. It shows the reverse trend and it is maximum at 0.007 M.



It is also found to increase with increasing concentration and leads to expansion of volume. It indicates intermolecular hydrogen bonding interaction at all the concentrations between the unlike molecules.

Conclusion

From the above observation, it may be concluded that intermolecular interaction takes place in this system. The increase in free length (L_f) with increase in the concentration of solute at 303.15 and 308.15 K indicates that there is a weak solute-solvent interaction. The increase in intermolecular free length at 0.005 M, 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. This may also imply the increase in number of free ions, showing the occurrence of ionic dissociation due to weak solute-solute interaction, while the free

TABLE-2
 IMPEDANCE (Z), RELAXATION TIME (τ), INTERACTION PARAMETER (χ_i), LENORD JONES POTENTIAL (LJP),
 COHESIVE ENERGY (CE) AND FREE ENERGY OF ACTIVATION (ΔG^\ddagger) FOR EQUIMOLAR CONCENTRATION
 OF CROTONALDEHYDE WITH ACETONE IN HEXANE SOLUTIONS AT 298.15, 303.15 AND 308.15 K

Conc. (M)	Impedance (Z) $10^5 \text{ Kg}^{-1} \text{ m}^2 \text{ s}^{-1}$			Relaxation time (ζ) 10^{-13} S			Interaction parameter (χ_i)		
	298.15 K	303.15 K	308.15 K	298.15 K	303.15 K	308.15 K	298.15 K	303.15 K	308.15 K
0.001	7.220	7.116	6.998	7.220	9.4065	8.9938	0.0197	-0.0204	-0.0565
0.002	7.222	7.101	7.027	7.222	8.9920	9.1357	0.0192	-0.0260	-0.0495
0.003	7.213	7.108	6.997	7.213	8.8652	9.1826	0.0207	-0.0200	-0.0574
0.004	7.208	7.130	7.033	7.208	8.8043	8.9164	0.0188	-0.0197	-0.0429
0.005	7.231	7.124	7.001	7.231	8.8391	9.1340	0.0241	-0.0209	-0.0543
0.006	7.208	7.110	7.022	7.208	8.8464	8.9905	0.0173	-0.0230	-0.0482
0.007	7.223	7.106	7.038	7.223	8.8432	8.8957	0.0200	-0.0245	-0.0435
0.008	7.217	7.094	7.014	7.217	8.8963	9.1952	0.0204	-0.0268	-0.0561
0.009	7.215	7.109	7.011	7.215	8.7735	9.0697	0.0186	-0.0248	-0.0531
0.010	7.191	7.105	7.044	7.191	8.7800	9.2675	0.0143	-0.0214	-0.0463
	Lenord jones potential (LJP)			Cohesive energy (CE) 10^4 KJ/Mol			Free energy of activation (ΔG^\ddagger) $10^{-19} \text{ KJ mol}^{-1}$		
0.001	5.684	4.931	4.291	3.8372	4.0190	3.9587	3.93181	4.00032	4.06373
0.002	5.675	4.831	4.413	3.8520	3.9244	3.9976	3.93213	3.99844	4.06440
0.003	5.706	4.941	4.279	3.8538	3.9014	3.9996	3.93216	3.99784	4.06461
0.004	5.666	4.942	4.528	3.8535	3.8899	3.9543	3.93219	3.99756	4.06336
0.005	5.776	4.927	4.335	3.8325	3.8967	3.9918	3.93162	3.99772	4.06439
0.006	5.644	4.890	4.442	3.7594	3.8957	3.9665	3.93016	3.99776	4.06372
0.007	5.699	4.864	4.525	3.7855	3.8937	3.9504	3.93067	3.99774	4.06326
0.008	5.708	4.824	4.307	3.7891	3.9029	4.0053	3.93075	3.99799	4.06467
0.009	5.673	4.860	4.359	3.7982	3.8786	3.9797	3.93098	3.99741	4.06409
0.010	5.592	4.924	4.480	3.7873	3.8820	4.0310	3.93084	3.99744	4.06501

length (L_f) indicates solute-solvent interaction. This may be due to the decrease in number of free ions, showing the occurrence of ionic association due to solute-solvent interaction.

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