Research Article

Ultrasonic Study of Molecular Interaction between Acetophenone and Benzaldehyde in n-hexane at Different Temperatures

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ABSTRACT

Densities, absolute viscosities and ultrasonic velocities of ternary mixtures of benzaldehyde in acetophenone have been measured for the ternary mixtures at 298K, 303K, 308K and 313K 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 variation in ultrasonic velocity depends on the intermolecular free length on mixing. The results have been interpreted in terms of specific intermolecular interactions present in the mixtures and are found to support each other.

Keywords: adiabatic compressibility, free length, relaxation time.

INTRODUCTION

Properties of liquid–liquid mixtures are thermodynamically very essential as component of studies of the acoustic, thermodynamic and transport aspects. In the present work, an attempt has been made by studying the temperature dependence of different parameters on the strength of molecular interactions of some organic liquid mixtures. Acetophenone can forms charge transfer complexes with electron donors.[1] Acetophenone is used in the production of cosmetics and fruit flavouring agents. Acetophenone is an important industrial chemical widely used as an ingredient of flavor and fragrance in detergents, soaps and perfumes. 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). 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 dynamics.[2] Molecular interaction studies as functions of concentration scale are useful in giving insight into the structure and bonding of associated molecular complex and other molecular processes[4].

MATERIALS AND METHODS

Experimental method

The chemicals used were of analytical grade and obtained from E.Merck company. Thermostatically controlled well-stirred water bath whose temperature was maintained to ±0.01 K accuracy was used for all the measurements. Binary mixtures were prepared by weighing in airtight bottles. In the present work, the densities (ρ) and ultrasonic velocities (U) of ternary mixtures of benzaldehyde with acetophenone in hexane at 298, 303.15 and 308.15K 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 $1x10^{-2}$M to $1x10^{-3}$M. The ultrasonic velocity in ternary mixtures have been measured using an ultrasonic interferometer (Mittal type-Model: F81) working at a frequency of 2MHz with an overall accuracy of ± 2 ms^{-1}. The density and viscosity are measured using a specific gravity bottle and an Ostwald's viscometer with an accuracy of ± 0.1 mg and ± 0.001 Nsm^{-2} respectively.[3] 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 ±0.1°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.

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

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

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

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).[4]

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 ----- (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 298.15K, 303.15K and 308.15K.

RESULTS AND DISCUSSION

The experimental data of density, ultrasonic velocity, viscosity, and other acoustical parameters such as adiabatic compressibility(κ), intermolecular free length(L_f), specific acoustic impedance(Z), molecular interaction parameter(χ_u), absorption co-efficient(α/f^2), relaxation time(τ), molar volume (V_m), available volume(V_a), free volume(V_f), internal pressure(π_i), molar cohesive energy(MCE), Lenard Jones Potential(LJP), free energy of formation (ΔG^*), and surface tension(σ) of acetophenone (acceptor) with benzaldehydes donor compound in n-hexane solution at equimolar concentration at varying temperatures of 293, 298K, 303 and 308K are presented in tables 1.1-1.2.

The plots of ultrasonic velocity versus concentration are shown in Fig 1.1. It is found that the ultrasonic velocity gradually increases in with increase in concentration. As the temperature increases, the velocity decreases were studied. Adiabatic compressibility (κ) shows an inverse behavior for each systems as shown in Fig. 1.2. In a given system, the κ and L_f values slightly decreases with increase in concentration. The decrease in compressibility signifies strong molecular interaction. It is observed that the intermolecular free length values linear by increases with temperatures as shown in Fig.1.3. Similar trend is observed for the intermolecular free length values for each system studied. The decrease in L_f with concentration further indicated decrease in intermolecular free length of the ternary mixtures, which supports that the benzaldehyde with acetophenone with solvent interaction increases with increase in concentration. The variation in free length with concentration shows a similar performance to that of the adiabatic compressibility. These results are supported by the decrease in velocity in the donor-acceptor complex.[5] This change in density and viscosity may be due to thermal effect of the molecular of the components with increase in temperature. The Plots of acoustic impedance versus concentration are shown in Fig.1.4.

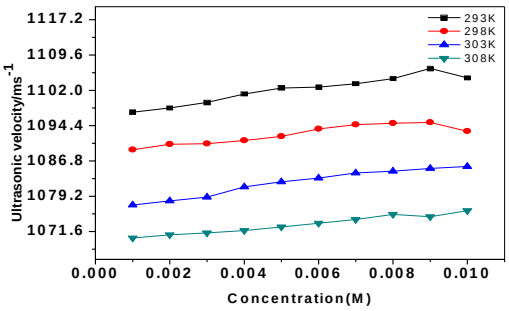

Figure 1.1: Plots of U Vs concentration for acetophenone + benzaldehyde system

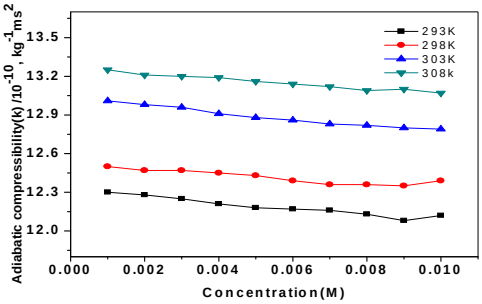

Figure 1.2: Plots of κ Vs concentration for acetophenone + benzaldehyde system

The value of Z increases with increase in concentration. As the temperature increases, the values of acoustical impedance decreases. It supports the possibility of complex formation between acetophenone and donor molecules in n-hexane medium in all the temperatures. The value of V_m shows linear effect. The value of molar volume increases with increase with increase in temperatures.[6] These values of α/f^2 and τ are computed from the ultrasonic viscosity, velocity and density.

It is observed that the values of α/f^2 and τ are slightly decreases with increase in concentration. It shows the intrinsic properties of the charge transfer complexation. When the temperature is increased, the values of α/f^2 and τ increases. It shows the non-linear variation. It is found that the internal pressure decrease with increase in concentration systems. The decreasing values of π_i indicates that molecular repulsive forces dominates.[7] It may form of weak charge transfer complexation between acetophenone and donor molecule. It suggests that the attractive forces dominates at higher concentration.

Cohesive energy in a liquid mixture is a calculate of intermolecular forces between the component molecules. It is found that the value of MCE decrease with increase in concentration.

The decreasing values of MCE indicates that molecular repulsive forces dominates. When the temperature increases, the molar cohesive energy decreases.

Table 1.1: Ultrasonic velocity(u), density(ρ), viscosity(η), adiabatic compressibility(κ), intermolecular free length(L_f), specific acoustic impedance(z), absorption co-efficient(α/f^2), molecular interaction parameter(χ_u) and relaxation time(τ) of acetophenone with benzaldehyde in n-hexane solution at equimolar concentration at 293 and 298K

*Conc., M	U ms^{-1}	ρ Kgm^{-3}	$\eta/10^{-4}$ Nsm^{-2}	$\kappa/10^{-10}$ $kg^{-1}ms^2$	$L_f/10^{-11}$m	$Z/10^4$ $Kgm^{-2}s^{-1}$	$\alpha/f^2/10^{-14}$ $Npm^{-1}s^2$	$\chi_u/10^{-2}$	$\tau/10^{-13}$ secs
293K									
0.001	1097.3	675.1	5.102	12.30	7.015	74.08	10.54	0.0406	8.369
0.002	1098.2	675.2	5.126	12.28	7.009	74.15	10.56	0.0421	8.393
0.003	1099.4	675.3	5.091	12.25	7.000	74.24	10.46	0.0442	8.316
0.004	1101.2	675.4	5.122	12.21	6.988	74.38	10.47	0.0474	8.339
0.005	1102.5	675.5	5.058	12.18	6.980	74.47	10.30	0.0497	8.213
0.006	1102.7	675.6	5.129	12.17	6.978	74.50	10.44	0.0499	8.324
0.007	1103.4	675.7	5.136	12.16	6.973	74.56	10.43	0.0510	8.325
0.008	1104.5	675.8	5.172	12.13	6.966	74.64	10.47	0.0529	8.365
0.009	1106.7	675.9	5.199	12.08	6.951	74.80	10.46	0.0569	8.374
0.010	1104.7	676.0	5.211	12.12	6.963	74.68	10.54	0.0529	8.422
298K									
0.001	1089.2	674.4	5.135	12.50	7.071	73.46	10.86	0.0253	8.557
0.002	1090.4	674.5	5.186	12.47	7.062	73.55	10.93	0.0273	8.621
0.003	1090.5	674.6	5.181	12.47	7.061	73.57	10.92	0.0273	8.611
0.004	1091.2	674.7	5.098	12.45	7.056	73.62	10.72	0.0285	8.460
0.005	1092.1	674.8	5.167	12.43	7.050	73.69	10.83	0.0300	8.559
0.006	1093.7	674.9	5.171	12.39	7.039	73.81	10.79	0.0328	8.540
0.007	1094.6	675	5.130	12.36	7.033	73.89	10.68	0.0343	8.457
0.008	1094.9	675.1	5.128	12.36	7.030	73.92	10.67	0.0347	8.447
0.009	1095.1	675.2	5.101	12.35	7.028	73.94	10.60	0.0349	8.400
0.010	1093.2	675.3	5.034	12.39	7.040	73.82	10.52	0.0311	8.317
303K									
0.001	1077.3	662.5	4.966	13.01	7.213	71.37	11.05	0.0030	8.612
0.002	1078.2	662.6	4.958	12.98	7.206	71.44	11.00	0.0045	8.583
0.003	1079.0	662.7	4.975	12.96	7.201	71.50	11.02	0.0057	8.598
0.004	1081.2	662.8	4.883	12.91	7.185	71.66	10.74	0.0097	8.402
0.005	1082.3	662.9	4.909	12.88	7.177	71.75	10.77	0.0116	8.429
0.006	1083.1	663.0	4.959	12.86	7.171	71.81	10.85	0.0129	8.501
0.007	1084.2	663.1	4.930	12.83	7.164	71.89	10.75	0.0148	8.432
0.008	1084.6	663.2	4.840	12.82	7.160	71.93	10.54	0.0153	8.272
0.009	1085.2	663.3	4.838	12.80	7.156	71.98	10.52	0.0163	8.259
0.010	1085.6	663.4	4.839	12.79	7.153	72.02	10.51	0.0168	8.253
308K									
0.001	1070.2	659.1	4.632	13.25	7.279	70.54	10.57	-0.0102	8.182
0.002	1070.9	660.0	4.521	13.21	7.270	70.68	10.28	-0.0091	7.964
0.003	1071.3	660.1	4.322	13.20	7.266	70.72	9.816	-0.0085	7.607
0.004	1071.8	660.2	4.154	13.19	7.262	70.76	9.420	-0.0078	7.303
0.005	1072.6	660.3	4.058	13.16	7.256	70.82	9.180	-0.0065	7.122
0.006	1073.4	660.4	4.121	13.14	7.250	70.89	9.301	-0.0052	7.221
0.007	1074.2	660.5	4.402	13.12	7.245	70.95	9.911	-0.0039	7.701
0.008	1075.3	660.6	4.401	13.09	7.237	71.03	9.877	-0.0020	7.683
0.009	1074.8	660.7	4.123	13.10	7.239	71.01	9.264	-0.0031	7.203
0.010	1076.1	660.8	4.212	13.07	7.230	71.11	9.429	-0.0009	7.339

*[Acetophenone] = [Benzaldehyde]

Table 1.2: The values of molar volume V_m, available volume V_a, free volume V_f, internal pressure π_i, molar cohesive energy MCE, Lenard Jones Potential LJP, molar sound velocity R, molar compressibility W, free energy of formation ΔG^* and surface tension σ of acetophenone with benzaldehyde in n-hexane solution at equimolar concentration at 293 and 298K

*Conc., M	$V_m/10^{-5}$ m^3mole^{-1}	$V_a/10^{-5}$ m^3mole^{-1}	$V_f/10^{-7}$ m^3mole^{-1}	$\pi_i/10^8$ atm	MCE/10^4 kJ mol^{-1}	LJP	R / 10^{-3}	W/ 10^{-3}	ΔG*/ 10^{-19}	σ
293K										
0.001	12.767	4.01	2.85	2.920	3.7	6.1	1.3	2.4	3.865	15460
0.002	12.766	4.00	2.83	2.926	3.7	6.1	1.3	2.4	3.865	15481
0.003	12.765	3.99	2.87	2.914	3.7	6.2	1.3	2.4	3.865	15509
0.004	12.764	3.98	2.85	2.921	3.7	6.2	1.3	2.4	3.865	15549
0.005	12.763	3.97	2.91	2.900	3.7	6.3	1.3	2.4	3.864	15579
0.006	12.762	3.97	2.85	2.920	3.7	6.3	1.3	2.4	3.865	15585
0.007	12.762	3.96	2.85	2.922	3.7	6.3	1.3	2.4	3.865	15602
0.008	12.761	3.95	2.82	2.930	3.7	6.4	1.3	2.4	3.865	15628
0.009	12.760	3.93	2.81	2.935	3.7	6.5	1.3	2.4	3.865	15677
0.010	12.759	3.95	2.79	2.941	3.8	6.4	1.3	2.4	3.865	15637
298K										
0.001	12.780	4.08	2.79	2.988	3.8	5.8	1.3	2.4	3.931	15273
0.002	12.779	4.07	2.76	3.001	3.8	5.8	1.3	2.4	3.931	15300
0.003	12.778	4.07	2.76	3.000	3.8	5.8	1.3	2.4	3.931	15305
0.004	12.777	4.06	2.83	2.975	3.8	5.9	1.3	2.4	3.931	15322
0.005	12.776	4.06	2.78	2.994	3.8	5.9	1.3	2.4	3.931	15343
0.006	12.776	4.04	2.78	2.993	3.8	6.0	1.3	2.4	3.931	15379
0.007	12.775	4.04	2.82	2.980	3.8	6.0	1.3	2.4	3.931	15400
0.008	12.774	4.03	2.82	2.978	3.8	6.0	1.3	2.4	3.931	15409
0.009	12.773	4.03	2.85	2.971	3.8	6.0	1.3	2.4	3.930	15415
0.010	12.772	4.05	2.90	2.954	3.8	5.9	1.3	2.4	3.930	15378
303K										
0.001	13.009	4.25	2.89	2.969	3.9	5.4	1.3	2.4	3.997	14758
0.002	13.008	4.24	2.90	2.966	3.9	5.4	1.3	2.4	3.996	14779
0.003	13.008	4.24	2.89	2.970	3.9	5.4	1.3	2.4	3.997	14797
0.004	13.007	4.22	2.98	2.939	3.8	5.5	1.3	2.4	3.996	14845
0.005	13.006	4.21	2.96	2.945	3.8	5.5	1.3	2.4	3.996	14870
0.006	13.005	4.20	2.92	2.959	3.8	5.6	1.3	2.4	3.996	14889
0.007	13.004	4.19	2.95	2.949	3.8	5.6	1.3	2.4	3.996	14914
0.008	13.003	4.19	3.03	2.921	3.8	5.6	1.3	2.4	3.995	14924
0.009	13.002	4.18	3.04	2.920	3.8	5.6	1.3	2.4	3.995	14939
0.010	13.001	4.18	3.04	2.920	3.8	5.7	1.3	2.4	3.995	14949
308K										
0.001	13.076	4.33	3.17	2.914	3.8	5.1	1.3	2.4	4.060	14537
0.002	13.060	4.32	3.30	2.881	3.8	5.1	1.3	2.4	4.059	14572
0.003	13.059	4.32	3.53	2.816	3.7	5.2	1.3	2.4	4.057	14582
0.004	13.058	4.31	3.75	2.760	3.6	5.2	1.3	2.4	4.055	14594
0.005	13.057	4.30	3.89	2.727	3.6	5.2	1.3	2.4	4.054	14613
0.006	13.056	4.30	3.80	2.747	3.6	5.2	1.3	2.4	4.054	14632
0.007	13.055	4.29	3.45	2.838	3.7	5.3	1.3	2.4	4.057	14650
0.008	13.054	4.28	3.45	2.837	3.7	5.3	1.3	2.4	4.057	14675
0.009	13.053	4.29	3.81	2.746	3.6	5.3	1.3	2.4	4.054	14667
0.010	13.052	4.27	3.69	2.774	3.6	5.3	1.3	2.4	4.055	14696

*[Acetophenone] = [Benzaldehyde]

The change in values of molar cohesive energy with concentration is similar to the trend in internal pressure. The available volume decreases with increase in concentration. The value of V_a increases with increase in temperatures. This is supported by the value of free length deviation related to tendency in available volume.

The magnitude of lennard jones potential is useful in finding the finding existing in liquid mixture is whether attractive or repulsive. The LJP values increases with increase in concentration. The values of LJP decrease with increase in temperatures. The variation of LJP values are similar of ultrasonic velocity. The values of surface tension increases with increase in concentration for all temperatures 293, 298, 303 and 308K. It is observed that the values of surface tension decreases with increase in temperature. It is investigated that the values of molar sound velocity and molar compressibility have very small deviation with concentration for the acetophenonene-carbonyl system. It shows that the charge transfer complexes arise between the acetophenone and benzaldehyde system.

CONCLUSION

The molecular interaction parameter is indicative of the extent of the degree of deviation of velocity from ideal behavior. These values can be used to evaluate the strength of molecular association between acetophenone and donor molecules in non-polar medium like n-hexane. Negative values are observed for acetophenone-benzaldehyde at 308K in higher concentration. Positive values of molecular interaction parameter shows that the less stable complex may be formed. The negative value of molecular interaction parameter shows the extent of complexation.

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