

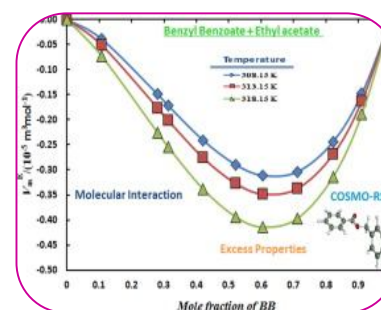


INVESTIGATION OF MOLECULAR INTERACTIONS WITH ADDITION OF 3-PHENYL-1- (3-BROMOPHENYL) PROP-2-EN-1-ONE IN MIXED SOLVENTS AT VARIOUS TEMPERATURES: AN INSIGHT FROM ULTRASONIC SPEED OF SOUND AND DENSITY

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ABSTRACT

3-phenyl-1- (3-bromophenyl) prop-2-en-1-one have been synthesized and characterized by M.P., Infrared spectroscopy, Thin Layer Chromatography, and H^1 NMR and GCMS data. The ultrasonic velocity and refractive indices of mixed solvents 0-100% (by wt.) of 3-phenyl-1- (3-bromophenyl) prop-2-en-1-one have been measured at three different temperatures 298, 303, and 308K. The experimental data obtained was used to calculate various parameters such as Molar volume (V_m), Free volume (V_f), Acoustical impedance (Z), intermolecular free path length(L_f), adiabatic compressibility(β), Rao's molar sound velocity (R_m), Relative association (R_a) Molar refraction (R_m), Specific refraction (r) and Polarisability constant(α).

These parameters are interpreted in terms of solute- solute and solute- solvent interaction and its effect on mixed solvent systems.

KEY WORDS: Refractive index, Mole fraction, Polarisability, Molar refraction, molar volume, Relative association, ultrasonic velocity

1. INTRODUCTION:

The drug solvent interaction is of great theoretical and practical importance. The thermodynamic and acoustical properties give qualitative information about intermolecular forces in the solutions are calculated from the speed of sound and density.

Ultrasonic methods find extensive applications for characterizing aspects of physicochemical behavior such as the nature of molecular interactions in pure liquids as well as liquid mixtures^[1-5]. Such studies as a function of concentrations are useful in gaining insight into the structure and bonding of associated molecular complexes and other molecular processes^[5-10]

Ultrasonic velocity measurements have been successfully employed to detect and assess weak and strong molecular interactions which are present in binary and ternary liquid mixtures. In this paper, an attempt is made to investigate the ultrasonic studies of 3-phenyl-1- (3-bromophenyl) prop-2-en-1-one in methanol and benzene binary liquid mixture systems at 298,303 and 308 K are made.

2. EXPERIMENTAL:

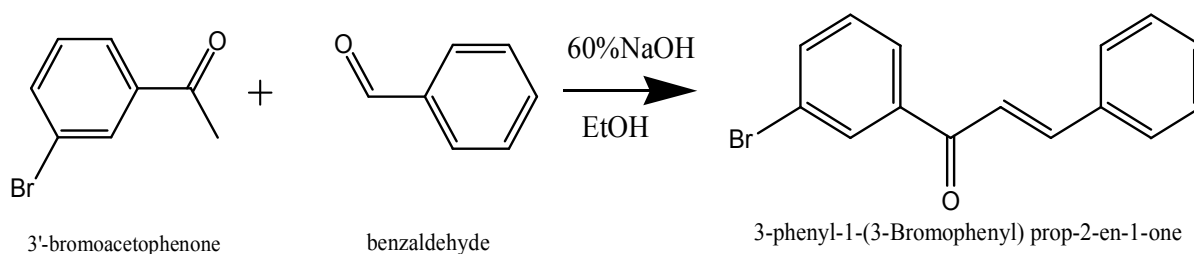
All the chemicals used in present work were analytical reagent (AR) grade (99.9% pure) and were supplied by SD fine chemicals Ltd India. Ultrasonic velocities were measured with ultrasonic interferometer (model F 80) supplied by Mittal enterprises, New Delhi, operating at a frequency of 2 MHz. with an accuracy of $\pm 0.1\%$. Viscosities of pure solvents and their mixtures were determined using Ostwald's viscometer with an accuracy of $\pm 0.002\%$, calibrated with double distilled water. The densities of pure compounds and their

solutions were measured accurately using 10 ml specific gravity bottles in ANAMED electric balance precisely and the accuracy in weighing is ± 0.1 mg.

Abbe's Refractometer having accuracy with was used for the measurement of refractive Index. The temperature of prism box was maintained constant by circulating water from thermostat at 298,303,308K

3. SYNTHESIS:

A mixture of 3'-bromoacetophenone (10 mmol) and benzaldehyde (10 mmol) was stirred for 24 hours in presence of NaOH as a catalyst. The product was isolated and recrystallised from ethanol. The purity of compound was checked by Thin Layer chromatography, Melting point. And the characterization of synthesized compound was done by IR, NMR and GCMS data.



4. RESULTS AND DISCUSSIONS:

Various parameters such as adiabatic compressibility (β) free path length (L_f) and acoustical impedance (Z)^[11] were calculated from the measured data using the following standard expressions.

$$\text{Adiabatic compressibility } (\beta) = \frac{1}{U^2 \times \rho}$$

$$\text{Intermolecular Free path length } (L_f) = K_j \times \beta^{1/2}$$

Where K_j = Jacobson's constant = 6.0816×10^4

$$\text{Acoustical Impedance } (Z) = U \times \rho$$

By using the density, viscosity, and sound velocity some thermodynamic parameters were determined by following relations

Effective molecular mass (M_{eff}),

$$M_{eff} = \sum X_i M_i$$

Where, X_i = Mole fraction and M_i = molecular weight of i^{th} component.

The Molar compressibility or Wada's constant^[12] can be calculated by equation,

$$W = \frac{M}{\rho} \times \beta^{-\frac{1}{7}}$$

Where, M = relative molar mass and β = compressibility factor.

The Molar refraction of solvent and solution mixtures were determined from,

The Molar refraction^[13-15] of binary liquid mixtures such as methanol-benzene mixture were determined from,

$$R_{M-B} = \frac{n^2 - 1}{n^2 - 2} \times \{(x_1 m_1 + x_2 m_2) | d\}$$

Where,

Rm= Molar Refraction	X ₁ = Mole fraction of solvent
n = R.I of Solution	X ₂ = Mole fraction of solution
M ₁ , M ₂ = Molecular Weights of solvent	D = Density of solution.

The Polarisability constant ^[16] (α) of solution is calculated from equation,

$$\alpha = \frac{3 Rm}{4 \pi N_0}$$

Where, α = Molar Polarisability N₀= Avogadro’s number = 6.023 X 10²³

The molar volume ^[17] (V_m) can be calculated by the relation,

$$V_m = \frac{M_{eff}}{\rho_0}$$

Similarly, Free Volume,

$$V_f = \frac{(M_{eff} \times U)^{\frac{3}{2}}}{K \eta}$$

Where, K= 4.028 ×10⁹ for all liquids which is a temperature independent constant.

The Rao’s molar sound function ^[18] (R_m) was calculated by equation,

$$R_m = \frac{M_{eff} \times U}{K \times \eta}$$

Viscous relaxation time ^[17] (τ):

$$\text{Viscous relaxation time } (\tau) = 4\tau/3pU^2$$

Gibb’s Free Energy ^[19] (ΔG*):

The relaxation time for a given transition is related to the activation free energy. The variation of KT with temperature can be expressed in the form of Eyring salt process theory.

$$1/\tau = KT/h \exp - (\Delta G^*/KT)$$

The above equation can be rearranged as,

$$\Delta G^* = KT \log h / KT \tau$$

Where K is the Boltzmann constant and h is plank’s constant.

all these parameters are calculated and listed in the tables 1.1,1.2,1.3 at temperature 298K tables 2.1, 2.2, 2.3 at 303K and 3.1, 3.2, 3.3 at temperature 308K respectively.

5. Tables:

Table No.1.1: Acoustical Parameters of 3-phenyl-1- (3-bromophenyl) prop-2-en-1-one in Benzene + Methanol mixture at 298K.

% of Methanol (by weight)	Mole Fraction		Density (ρ) g cm^{-3}	Ultrasonic velocity(U) ms^{-1}	Effective Molecular Weight (M_{eff})	Molar volume (V_m) $\text{m}^3\text{mol}^{-1}$	Rao's molar sound velocity (Rm) m/s
	X_1	X_2					
0	0.0000	1.0000	0.8698	1255.5	78.000	89.760	980.52
10	0.1977	0.8022	0.86	1236.2	68.900	80.110	862.94
20	0.3568	0.6432	0.8529	1219.2	61.587	72.210	774.64
30	0.4874	0.5128	0.8465	1193.6	55.578	65.657	701.13
40	0.5966	0.4034	0.8408	1191.5	50.555	60.125	638.59
50	0.6893	0.3107	0.8331	1190.7	46.293	55.566	588.64
60	0.7689	0.2310	0.8263	1163.2	42.628	51.587	545.75
70	0.8381	0.1619	0.8195	1145.1	39.447	48.133	506.23
80	0.8987	0.1013	0.8131	1135.6	36.660	45.085	472.93
90	0.9523	0.0477	0.8056	1124.7	34.194	42.445	443.11
100	1.0000	0.0000	0.7889	1092.0	32.000	40.562	420.17

Table No. 1.2: Acoustical Parameters of 3-phenyl-1- (3-bromophenyl) prop-2-en-1-one in Benzene + Methanol mixture at 298K.

Wt. % of methanol	Adiabatic compressibility (β) $\times 10^{-7}$ $\text{Kg}^{-1}\text{ms}^{-2}$	Free path length (Lf) $\times 10^{-8}$ m	Acoustical impedance (Z) $\text{Kg.m}^{-2}\text{s}^{-1}$	Refractive Index (n)	Wada's constant (W)	Relative association (Ra)	Molar sound velocity (Rm)
0	6.772	3.1984	1132.8	1.4915	105705	1.0081	972.640
10	6.478	3.4750	1152.2	1.4645	92438.8	1.0025	863.940
20	7.691	3.7259	1052.1	1.4510	81791.9	0.9998	774.312
30	7.966	4.1343	1030.8	1.4360	72624.5	0.9971	700.687
40	8.285	4.2221	1007.4	1.4240	66179.3	0.9905	641.510
50	8.492	4.3178	990.48	1.4085	60825.8	0.9818	592.732
60	8.633	4.7976	978.37	1.3960	54919.4	0.9827	545.265
70	9.016	5.2041	953.42	1.3820	50284.5	0.9784	506.870
80	9.231	5.4628	945.95	1.3695	46500.1	0.9738	473.124
90	9.589	5.7758	916.59	1.3550	43153.2	0.9654	443.803
100	10.26	6.7690	876.92	1.3270	39626.6	0.9580	419.905

Table No.1.3: Density, Refractive Index, Molar Refraction, and Polarizability Constant of 3-phenyl-1- (3-bromophenyl) prop-2-en-1-one in Benzene + Methanol mixture at 298K

% of Methanol (by weight)	Density gm/cm ³	Refractive index (n)	Internal pressure (π_i) $\times 10^3$ atm	Molar Refraction (R _m)	Polarizability constant (α) $\times 10^{-23}$
0	0.8665	1.4750	1.3578	25.340	1.0050
10	0.8573	1.4625	1.1687	22.115	0.8770
20	0.8511	1.4500	1.1861	19.446	0.7712
30	0.8428	1.4350	1.8879	17.207	0.6824
40	0.8368	1.4220	2.1657	15.351	0.6087
50	0.8291	1.4060	2.3710	13.715	0.5438
60	0.8236	1.3940	2.5786	12.381	0.4910
70	0.8157	1.3800	2.8754	11.203	0.4443
80	0.8096	1.3670	3.1021	10.165	0.4031
90	0.8027	1.3550	3.2614	9.2840	0.3682
100	0.7862	1.3260	3.4751	8.2121	0.3256

Table No.2.1: Acoustical Parameters of 3-phenyl-1- (3-bromophenyl) prop-2-en-1-one in Benzene + Methanol mixture at 303K.

% of Methanol (by weight)	Mole fraction		Density (ρ) g cm ⁻³	Ultrasonic velocity (U) ms ⁻¹	Effective Molecular Weight (M _{eff})	Molar volume (V _m) m ³ mol ⁻¹	Rao's molar sound velocity (R _m) m/s
	X ₁	X ₂					
0	0.0000	1.0000	0.8585	1255.5	78.000	89.760	980.15
10	0.1977	0.8022	0.8529	1215.2	68.900	80.110	862.06
20	0.3568	0.6432	0.8476	1206.8	61.587	72.210	773.59
30	0.4874	0.5128	0.8408	1192.8	55.578	65.657	701.05
40	0.5966	0.4034	0.8345	1182.0	50.555	60.125	640.47
50	0.6893	0.3107	0.8285	1163.6	46.293	55.566	587.69
60	0.7689	0.2310	0.8208	1155.6	42.628	51.587	544.99
70	0.8381	0.1619	0.8137	1142.8	39.447	48.133	506.88
80	0.8987	0.1013	0.8063	1141.2	36.660	45.085	475.00
90	0.9523	0.0477	0.7968	1129.2	34.194	42.445	446.88
100	1.0000	0.0000	0.7843	1108.8	32.000	40.562	422.30

Table No.2.2: Acoustical Parameters of 3-phenyl-1- (3-bromophenyl) prop-2-en-1-one in Benzene + Methanol mixture at 303K.

Wt. % of methanol	Adiabatic compressibility (β) $\times 10^{-7}$ Kg ⁻¹ ms ⁻²	Free path length (Lf) $\times 10^{-9}$ m	Acoustical impedance (Z) Kg.m ⁻² s ⁻¹	Refractive Index (n)	Wada's constant (W) $\times 10^{-3}$	Relative association (Ra)	Molar sound velocity (Rm)
0	7.3896	5.1732	1077.84	1.4810	105692.4	1.00037	972.640
10	7.9397	5.3620	1036.44	1.4645	90660.69	1.00472	863.940
20	8.1010	5.4165	1022.88	1.4490	80728.85	1.00078	774.312
30	8.3593	5.5022	1002.90	1.4350	72300.43	0.99660	700.687
40	8.5770	5.5734	986.38	1.4220	65407.43	0.99216	641.510
50	8.9150	5.682	964.04	1.4050	59176.97	0.99019	592.732
60	9.1230	5.7480	948.51	1.3940	54373.68	0.98320	545.265
70	9.4101	5.8378	929.89	1.3790	49978.77	0.97837	506.870
80	9.5260	5.8736	920.15	1.3665	46571.69	0.96990	473.124
90	9.8420	5.9702	899.76	1.3540	43256.70	0.96190	443.803
100	10.371	6.1286	869.63	1.3240	40064.28	0.95256	419.905

Table No.2.3: Density, Refractive Index, Molar Refraction, and Polarizability Constant of 3-phenyl-1- (3-bromophenyl) prop-2-en-1-one in Benzene + Methanol mixture at 303K.

% of Methanol (by weight)	Density gm/cm ³	Refractive index (n)	Internal pressure (π_i) $\times 10^3$ atm	Molar Refraction (R _m)	Polarizability constant (α) $\times 10^{-23}$
0	0.8585	1.4800	1.3387	25.856	1.0254
10	0.8529	1.4650	1.5310	22.312	0.8848
20	0.8476	1.4500	1.7655	19.489	0.7729
30	0.8408	1.4350	1.9347	17.249	0.6840
40	0.8345	1.4215	2.1345	15.393	0.6104
50	0.8285	1.4060	2.3220	13.695	0.5431
60	0.8208	1.3930	2.5323	12.423	0.4926
70	0.8137	1.3780	2.7443	11.204	0.4443
80	0.8063	1.3650	2.9716	10.194	0.4043
90	0.7968	1.3530	3.1802	9.3289	0.3699
100	0.7843	1.3240	3.6475	8.0860	0.3246

Table No.3.1: Acoustical parameters of 3-phenyl-1- (3-bromophenyl) prop-2-en-1-one in Benzene + Methanol mixture at Temperature 308K

% of Methanol (by weight)	Mole Fraction		Density (ρ) g cm^{-3}	Ultrasonic velocity (U) ms^{-1}	Effective Molecular Weight (M_{eff})	Molar volume (V_m) $\text{m}^3 \text{mol}^{-1}$	Rao's molar sound velocity (Rm) m/s
	X_1	X_2					
0	0.0000	1.0000	0.8569	1217.8	78.000	89.760	972.05
10	0.1977	0.8022	0.8512	1202.0	68.900	80.110	860.64
20	0.3568	0.6432	0.8450	1185.2	61.587	72.210	771.31
30	0.4874	0.5128	0.8379	1172.0	55.578	65.657	699.36
40	0.5966	0.4034	0.8311	1160.8	50.555	60.125	639.22
50	0.6893	0.3107	0.8236	1145.2	46.293	55.566	588.05
60	0.7689	0.2310	0.8175	1136.0	42.628	51.587	544.08
70	0.8381	0.1619	0.8096	1122.2	39.447	48.133	506.37
80	0.8987	0.1013	0.8032	1109.2	36.660	45.085	472.34
90	0.9523	0.0477	0.7961	1099.6	34.194	42.445	443.33
100	1.0000	0.0000	0.7812	1074.8	32.000	40.562	419.58

Table No.3.2: Acoustical Parameters of 3-phenyl-1- (3-bromophenyl) prop-2-en-1-one in Benzene + Methanol mixture. at temperature 308K.

Wt. % of methanol	Adiabatic compressibility (β) $\times 10^{-7} \text{Kg}^{-1} \text{ms}^{-2}$	Free path length (Lf) $\times 10^{-9} \text{m}$	Acoustical impedance (Z) $\text{Kg.m}^{-2} \text{s}^{-1}$	Refractive Index (n)	Wada's constant (W) $\times 10^{-3}$	Relative association	Molar sound velocity (Rm)
0	7.8690	5.3384	1043.53	1.4800	102613.5	1.0087	972.05
10	8.1313	5.4266	1023.14	1.4650	89765.12	1.0064	860.64
20	8.4250	5.5237	1001.49	1.4500	79404.91	1.0037	771.31
30	8.6880	5.6093	982.02	1.4350	71164.99	0.9990	699.36
40	8.9290	5.6866	964.74	1.4215	64367.47	0.9941	639.22
50	9.2580	5.7904	943.18	1.4060	58415.89	0.9896	588.05
60	9.4788	5.8590	928.68	1.3930	53558.76	0.9848	544.08
70	9.8082	5.9600	908.53	1.3780	49201.89	0.9793	506.37
80	10.119	6.0530	890.90	1.3650	45359.98	0.9754	472.34
90	10.388	6.1340	875.39	1.3530	42140.70	0.9696	443.33
100	11.081	6.3349	839.65	1.3240	38912.32	0.9587	419.58

Table No. 3.3: Density, Refractive Index, Molar Refraction, and Polarizability Constant of 3-phenyl-1- (3-bromophenyl) prop-2-en-1-one in Benzene + Methanol mixture at 308K

% of Methanol (by weight)	Density gm/cm ³	Refractive index (n)	Internal pressure (π_i) $\times 10^3$ atm	Molar Refraction (R _m)	Polarizability constant (α) $\times 10^{-23}$
0	0.8569	1.4800	1.3326	25.850	1.0250
10	0.8512	1.4650	1.5011	22.377	0.8874
20	0.8450	1.4500	1.7310	19.586	0.7767
30	0.8379	1.4350	1.9139	17.309	0.6864
40	0.8311	1.4215	2.1339	15.440	0.6123
50	0.8236	1.4060	2.3606	13.806	0.5475
60	0.8175	1.3930	2.5867	12.445	0.4935
70	0.8096	1.3780	2.8062	11.234	0.4455
80	0.8032	1.3650	3.0414	10.196	0.4043
90	0.7961	1.3530	3.2618	09.313	0.3693
100	0.7812	1.3240	3.4808	08.218	0.3259

6. CONCLUSION:

Many thermodynamic properties can be elucidated from ultrasound velocity, viscosity and density data. Thermodynamic data are very important tool for understanding molecular interaction; solute – solvent and solute – solute, occurring in the solution.

In the present paper, we have used this technique for the better understanding of molecular interaction in some solutions. The result is interpreted in terms of molecular interaction occurring in the solution.

The decrease in ρ , n and U with C suggest that the increase of cohesive forces is due to powerful molecular interactions^[20-22], while the decrease of these parameters with T indicates that the cohesive forces are decreased.

With a view to understand the effect of concentration, temperature, nature of solvents and structure of 3-phenyl-1- (3-bromophenyl) prop-2-en-1-one on structure of forming or structure – breaking tendency various acoustical parameters like acoustical impedance (Z), adiabatic compressibility (β), Intermolecular free path length (L_f), Internal pressure (π_i), Free volume (V_m) were determined by using the experimental data of ρ , n and U of 3-phenyl-1- (3-bromophenyl) prop-2-en-1-one solution in methanol and benzene at three different temperatures. All these parameters are calculated and listed in the tables 1.1, 1.2, 1.3 at temperature 298K and tables 2.1, 2.2, 2.3 and 3.1, 3.2, 3.3 for the temperature 303 and 308K respectively.

The Intermolecular free path length (L_f) is observed to increase with T suggesting the presence of solvent – solute interactions.

The increase of adiabatic compressibility (β) might be due to dissociation of solvent molecules around solute molecules supporting strong solvent-solute interactions^[23-25]. The adiabatic compressibility (β) of the solution of 3-phenyl-1- (3-bromophenyl) prop-2-en-1-one was also found to decrease with C and increase with T in system. These phenomena can be attributed to the solvated molecules that were fully compressed by electrical force of the ions. The compressibility of the solution was mainly due to free solvent molecules. The presence of compressibility of the solution increase with the decrease in solute concentration, due to solute-solvent interactions in the system. This was further confirmed by the increase in viscosity of 3-phenyl-1- (3-bromophenyl) prop-2-en-1-one solutions in methanol and benzene systems.

Increase of L_f with the C further supported solvent-solute interactions. Due to solvent-solute interactions, structural arrangement is considerably changed.

The internal pressure (π) is the resultant of forces of attraction and repulsion between the molecules in the solution. The result of adiabatic compressibility and intermolecular free path length. Which were found decreased with C and increased with T, while velocity and viscosity were found increased with C and decreased with T in methanol and benzene system, suggest that solute-solvent interaction is more predominant^[25-27].

This was confirmed from the results of internal pressure which was found to be increased. The internal pressure (π) of solution is single factor, which plays an important role in transport properties of solutions. The increase of internal pressure (π) and decrease of free volume (V_f) indicate that increase of cohesive forces and vice versa in the solutions.

The free volume (V_f) of a solute molecule at a particular temperature and pressure depend on the internal pressure of liquid in which it is dissolved. The decrease in free volume causes internal pressure decrease or vice versa however internal pressure increased and free volume decreased in both solvent systems. This again confirmed the existence of solute-solute and solute-solvent interactions in the system studied so far.

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