

Comparison between experimental result and theoretical prediction using Flory's theory for the binary liquid mixtures

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ABSTRACT

The velocity of ultrasonic (u.s) waves (10 MHz) for different compositions of mixtures of bio-liquids, Methanol, Cyclohexane and p-dioxane with Acrolein and Cinnamaldehyde has been measured in the temperature range 10-40⁰C. The percentage excess compressibility ($\% \beta_a^E$) and percentage excess molar volume ($\% V^E$) has been discussed in the light of intermolecular AB interactions and resulting disorder in these mixtures at temperature 303.15 K. Flory's theory has been applied in calculating u.s. velocity in mixture at temperature 303.15 K of molecular of different assigned shapes and good agreement between experiment and theory has been observed.

Keywords: Ultrasonic velocity, adiabatic compressibility, Flory's theory and molecular interaction.

INTRODUCTION

The liquid state exists relatively over a small portion of the huge range of temperature and pressure. However, it is of vital importance in science and technology and in various life process in the universe. Out of the three main states of matter, the liquid state is intermediate in its properties between solid and gas. Most attempts to develop a satisfactory theory of liquids states are directed towards simple consideration of molecular behaving like hard sphere, having attractive forces. But a large majority of liquids are complex and consist of poly-atomic, non-spherical molecule in which some additional molecular forces exist. Various theories have been applied to liquid molecules and equation states have been derived. The pioneering work of Vander Waal's led to a fairly good basic understanding of the static and dynamic physicochemical properties of liquids. Advances in statistical mechanics e.g. fundamental formulation of Gibb's and Boltzmann in integral equation and perturbation theory and techniques of computer simulation etc. have led to a better understanding of intermolecular forces in liquids. Ultimate aim of all studies is to get parameter characterizing liquid states, and the molecules forces existing between different types of component molecules, in the mixture of two or three

liquids. The work during last fifty years, in this field has developed a strong basis for predicating precise microscopic, static and dynamic properties of liquid. More recently an equation state has been derived by Khasare [1] which predicts the nature of interaction in liquid mixture.

In recent years, ultrasonic has become an important tool for studying physicochemical properties of matter. It finds tremendous applications in basic Science, industries and bio-medical technology. The characteristics of u.s. wave propagation, dispersion and attenuation in a medium are intimately connected with the structural aspect of the medium. The large number of theoretical modeling correlating the observed ultrasonic parameters with the structural arrangement of the constituent liquids and interaction among them, have proposed. Recent investigations of Sharada Ghosh [2] have shown the possibility of directly relating the gross u.s. parameter with the microscopic shape of interacting molecules in binary liquid mixtures. Thus the u.s. studies in liquids are of great use in knowing the nature and strength of reaction between liquid molecules in liquid mixtures.

In recent years, bio-liquids have attracted large attention from researchers all over the world. Ultrasonic studies are being carried out on a variety of liquids resembling bio-liquids. Bio-liquids [3] are made up of long chain molecules consisting of aromatic compounds. Bio-molecules are bigger in size are complicated in structure.

A review of literature [4] shows tremendous works on organic liquids, but scanty work on bio-liquids. Therefore it was thought worthwhile to undertake u.s. investigations of some bio-liquids. To understand the behavior of bio-molecules some representation, aliphatic, aromatic and α,β unsaturated carbonyl compounds namely cinnamaldehyde, Acrolein have been selected for the present study with the methanol p-dioxane and cyclohexane are solvent.

Methanol, p-dioxane, cinnamaldehyde, cyclohexane and Acrolein are bio-liquids. They are known to take active part in body metabolism. The methanol is a peculiar aliphatic alcohol with medicinal application. It affects nerves system and causes total blindness when taken in large amount. While p-dioxane and cyclohexane are alicyclic compounds, the cinnamaldehyde and Acrolein are α,β unsaturated carbonyl compounds. The α,β unsaturated carbonyl compounds are the topic of special interest and find application in Bio-medical technology and industries. To understand the behavior of α,β unsaturated carbonyl compounds, mainly cinnamaldehyde and Acrolein in the mixture with polar liquid methanol and non-polar liquid p-dioxane and cyclohexane as a solvent has been selected for experimental u.s. studies in the present work.

In a molecule containing different radicals, the relative orientation of the radicals is expected to play an important role in the interaction of these molecules with other polar and non-polar molecules. In the present study cinnamaldehyde, Acrolein, methanol and p-dioxane are oxygen bearing molecules while cyclohexane is a cyclic compound with closed ring.

A comparison of u.s. parameters of cinnamaldehyde and Acrolein in mixture with polar solvent methanol and non-polar solvent p-dioxane and cyclohexane was thought worthwhile. It was also intend to study whether this radicals in α,β unsaturated carbonyl compounds have a specific role to play in intermolecular interaction in binary mixtures. Most of the earlier theoretical u.s. work in found to be directly in predicting u.s. velocity using one or the other theories of liquid state. An attempt, has been made in present paper to calculate u.s. velocity from Flory's [5-7] theory using different shapes, such as spherical cubical, tetrahedral and disc for the molecule.

MATERIALS AND METHODS

The liquids methanol, p-dioxane, cinnamaldehyde, cyclohexane and Acrolein were of analar grade and redistilled before use. The binary mixture of different volume fraction of the two compounds was prepared immediately before use. The velocity of ultrasonic (u.s) waves at frequency 10 MHz and density in these mixtures were measured by employing ultrasonic time intervalometer UTI-101 (innovative instrument Hyderabad) and hydrostatic sinker method in the temperature range of 10-40⁰C. Ultrasonic U-10 maintained temperature of a sample constant to 0.1⁰C. A specially designed and fabricated double walled, metallic ultrasonic cell and glass cell along with six-digit monopan balance, permitted to achieve accuracy of 1 in 10⁴ gm in the density measurement. The ultrasonic velocity (u) and density (ρ) in these mixtures were found to be linear with temperature and hence method of least square was applied and values of u.s velocity (u) and density (u) at different temperature were calculated from the equation [8].

$$u(T) = u_0 + (du/dT) * T \quad \text{and} \quad \rho(T) = \rho_0 + (d\rho/dT) * T .$$

RESULTS AND DISCUSSION

The comparison of experimental velocity and theoretical velocity by Flory's theory with respect to the volume concentration (x) for the systems methanol+cinnamaldehyde, cyclohexane+cinnamaldehyde and p-dioxane + cinnamaldehyde and for the system methanol+Acrolein, cyclohexane+ Acrolein and p-dioxane+Acrolein respectively are shown in the Table-1 and Table-2 at the temperature 303.15 K.

On the basis of broad classification [8-15] of heteromolecular AB interaction, the systems under study has been classified into two categories namely, (case I) in which percentage excess volume (% V^E) and percentage excess compressibility (% β_a^E) are negative and case III) in which (% V^E) is positive and (% β_a^E) is negative are shown in the Fig-1 and Fig-2 respectively.

The (% V^E) and (% β_a^E) plots are found to be negative over the whole composition range (x) (fig-1) for the system, cyclohexane+ Acrolein and p-dioxane + cinnamaldehyde. This shows that, AB interaction in the above systems of attractive nature, therefore heteromolecular cluster occupies less volume than that of available volume. While the observed positive (% V^E) and negative (% β_a^E) variation over composition range (fig-2) in system, methanol+cinnamaldehyde, p-dioxane+Acrolein, cyclohexane +cinnamaldehyde and methanol +Acrolein respectively indicates the presence of dispersive type AB interactions. This further indicates the formation of big heteromolecular cluster.

The relative strength of AB interactions in this system is found to be decrease in the order, methanol+Acrolein, cyclohexane +cinnamaldehyde, Methanol+cinnamaldehyde, p-dioxane + cinnamaldehyde, cyclohexane+ Acrolein and p-dioxane+Acrolein respectively. Since the u.s. velocity and compressibility plots with compositions (cm) of all the systems are non-linear [9], indicating presence of heteromolecular AB interactions. No complex formation is observed in any of the systems.

The systems are classified into two categories namely case-1 in which V^E & β_a^E are negative (fig-1) and case-3 with (% V^E) is positive and (% β_a^E) is negative. According to broad classification. the system cyclohexane+ Acrolein and p-dioxane + cinnamaldehyde belongs to case-1 and p-dioxane+Acrolein, Methanol+cinnamaldehyde, cyclohexane +cinnamaldehyde and methanol+Acrolein belong to case-3 of broad classification (fig-2). The interaction in

cinnamaldehyde and Acrolein with methanol are of dipole-dipole type while with cyclohexane and p-dioxane are of dipole-induce dipole type.

Using Flory's Theory, theoretical u.s velocity [2] values are obtained from critical constant of the pure liquid. An equation of state [2, 5-7] for a liquid has been derived by assuming a molecule has hard convex sphere and the same is applied to the liquid mixture. A relation between u.s. velocity and molecular dimension, such as its radius of curvature, surface area and volume is established.

Table-1: Comparison of experimental velocity and theoretical velocity by Flory's theory w. r. to volume concentration (x) for the system cinnamaldehyde with methanol, cyclohexane and p-dioxane at 303.15 K.

X (cm)	cinna. + metha.		cinna. + cyclo.		cinna. + p-dioxane	
	sph. + tetra.		sph. + sph.		sph. + sph.	
	V (obs.)ms ⁻¹	V (Theo.)ms ⁻¹	V (obs.)ms ⁻¹	V (Theo.)ms ⁻¹	V (obs.)ms ⁻¹	V (Theo.)ms ⁻¹
0.1	1335.00	1332.13	1377.00	1380.27	1378.46	1377.12
0.2	1295.00	1289.63	1373.02	1373.39	1375.49	1376.11
0.3	1260.00	1261.09	1268.28	1360.16	1373.18	1374.21
0.4	1230.00	1231.77	1346.28	1343.14	1370.00	1371.80
0.5	1205.00	1204.30	1325.50	1325.63	1368.38	1367.59
0.6	1180.00	1182.53	1298.50	1306.62	1362.13	1362.32
0.7	1150.00	1150.49	1287.50	1288.88	1357.00	1356.48
0.8	1132.00	1136.36	1265.00	1271.11	1348.50	1347.59
0.9	1110.00	1116.85	1255.00	1255.59	1339.00	1336.75
AVE % DEV	= 0.3108		0.2500		0.0786	
Chi - Sq.	= 0.1364		0.1350		0.0122	

Table-2 : Comparison of experimental velocity and theoretical velocity by Flory's theory w. r. to volume concentration (x) for the system Acrolein with methanol, cyclohexane and p-dioxane at 303.15

X (cm)	acro. + metha.		acro. + cyclo.		acro. + p-dioxane	
	disc (b) + sph.		disc (b) + disc (d)		disc (c) + disc (d)	
	V (obs.)ms ⁻¹	V (Theo.)ms ⁻¹	V (obs.)ms ⁻¹	V (Theo.)ms ⁻¹	V (obs.)ms ⁻¹	V (Theo.)ms ⁻¹
0.1	1372.00	1371.34	1360.05	1364.97	1373.98	1395.08
0.2	1367.95	1369.96	1347.46	1350.46	1367.26	1371.42
0.3	1359.00	1364.73	1333.84	1335.21	1358.54	1365.41
0.4	1350.50	1355.18	1319.28	1319.43	1356.88	1358.48
0.5	1332.50	1339.20	1303.07	1304.53	1348.06	1350.91
0.6	1310.00	1310.20	1294.04	1290.48	1343.44	1343.44
0.7	1277.50	1272.85	1278.42	1278.05	1339.78	1336.38
0.8	1232.50	1223.30	1268.80	1264.56	1234.06	1339.64
0.9	1180.00	1161.41	1253.24	1252.64	1325.84	1324.46
AVE % DEV	= 0.4307		0.1528		0.2220	
Chi - Sq.	= 0.4301		0.0440		0.0830	

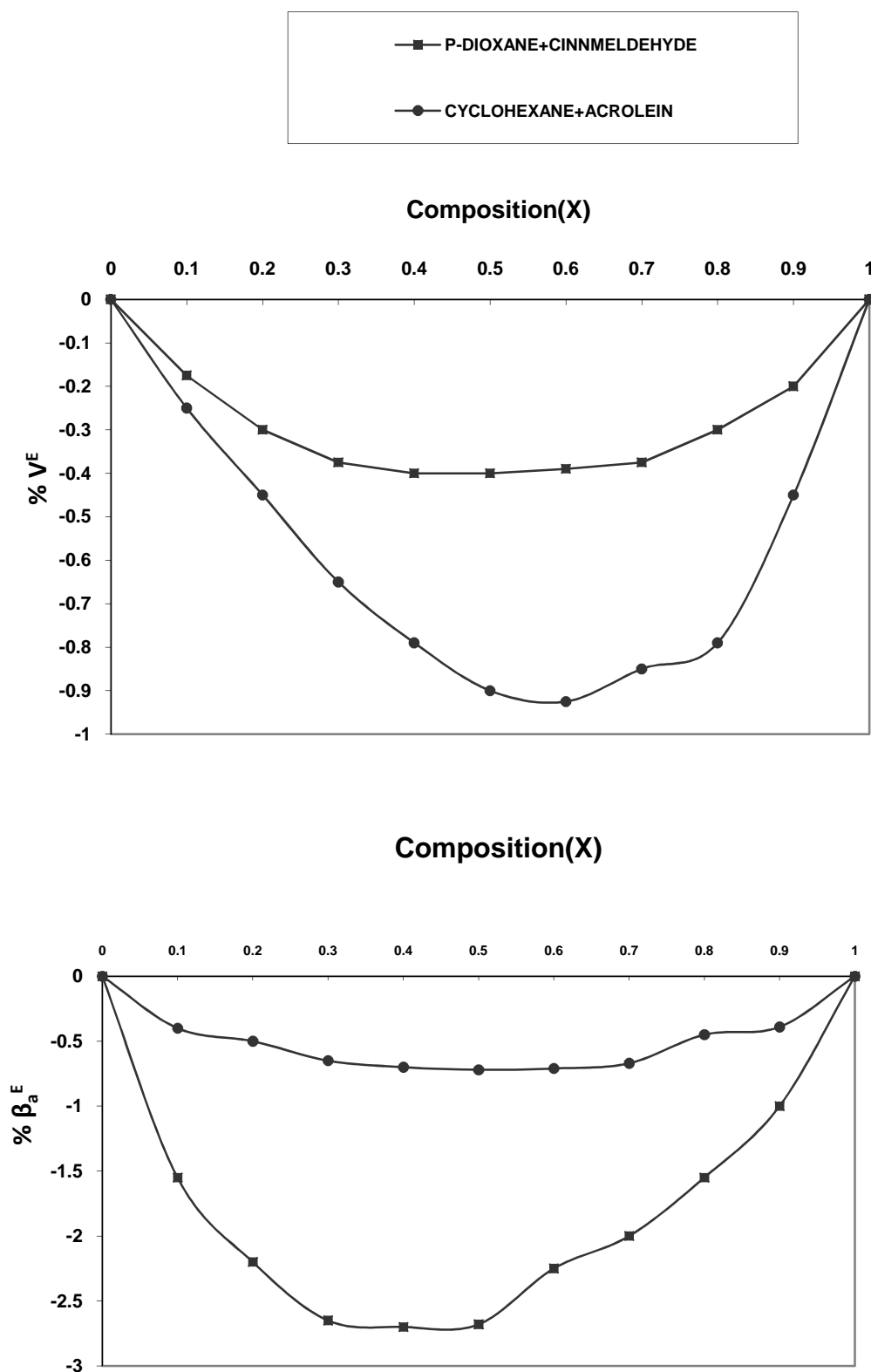


Fig. 1:- Variation of % V^E & % β_a^E w. r, to composition (X) of p- dioxane + Cinnamaldehyde & Cyclohexane + Acrolein.

Flory's theory has been applied in calculating u.s. velocity in mixture of molecules of different assigned shapes [9]. The u.s. Velocities obtained from Flory's theory are compared with experimental u.s. velocities and shown in Table-1 and Table-2. A good agreement between experimental and theoretical velocity is observed.

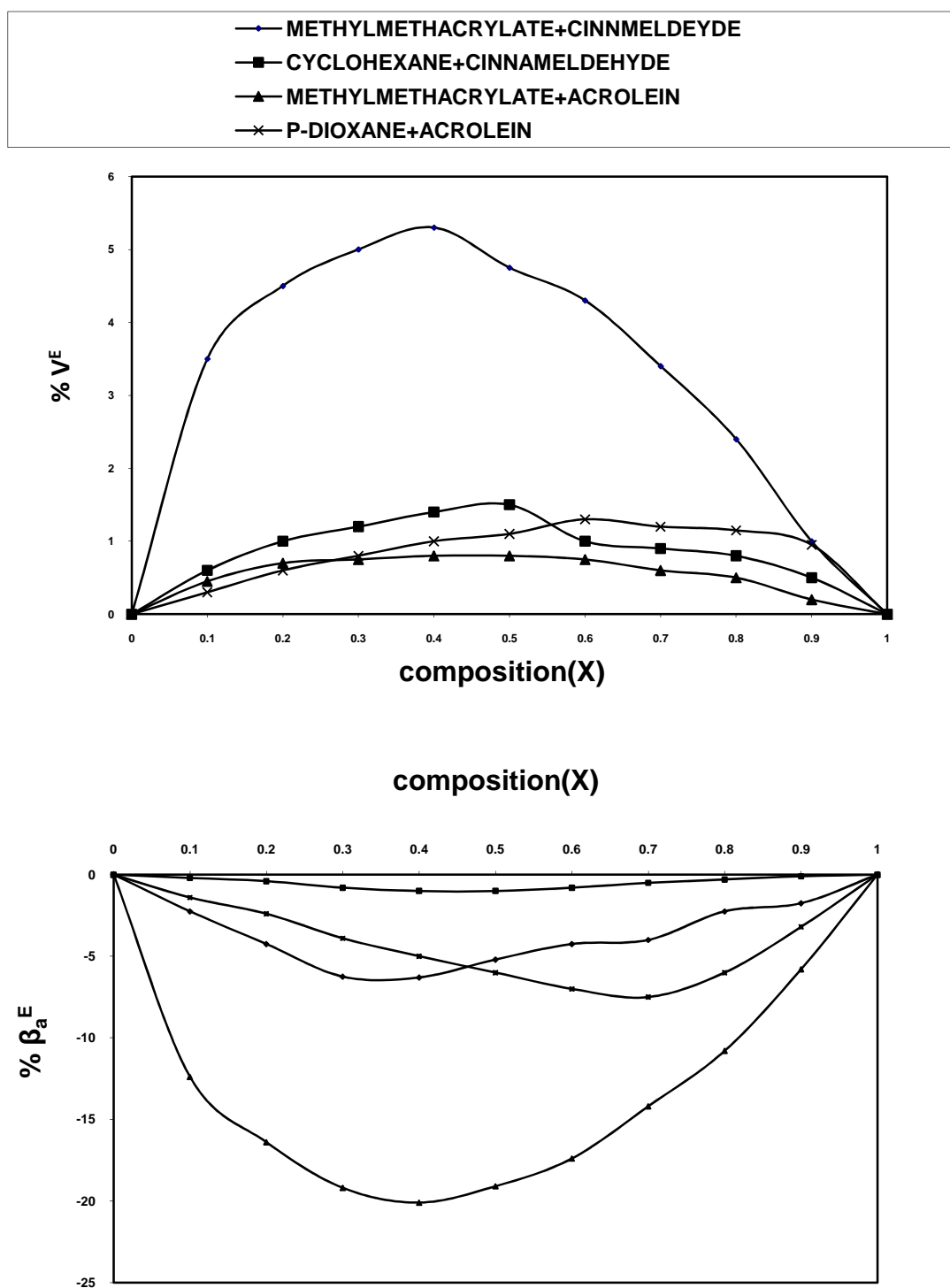


Fig. 2:- Variation of % V^E & % β_a^E w.r.to composition (X) of methanol + Cinnamaldehyde, cyclohexane + Cinnamaldehyde, methanol + Acrolein & p-dioxane + Acrolein.

CONCLUSION

The main conclusions of the present study, out lined in this paper are as follows:

- 1) The heteromolecular AB interaction is present in the system investigated, but no complex formation is observed.
- 2) The relative Strength of heteromolecular AB interaction in the system studies, decreases in the order of methanol+Acrolein, cyclohexane +cinnamaldehyde, methanol+cinnamaldehyde, p-dioxane + cinnamaldehyde, cyclohexane+ Acrolein and p-dioxane+Acrolein respectively.
- 3) The experimental velocities agree approximately with those calculated from Flory's theory.
- 4) When u.s. velocities are calculated from Flory's theory by introducing the concept of equivalent molecular radius, surface area and volume of sphere, even if, it has different shape such as cubical, tetrahedral, disc etc. The velocity data fits closely with experimental data. This help in assigning a particular shape to the interacting molecule in the mixture.
- 5) The Flory's theory is fund to predict the molecular shape of interacting molecule as follows:
 - a) Cinnamaldehyde ----- Disc (c)
 - b) Acrolein ----- Disc (b) or Disc (c)
 - c) Methanol ----- Tetrahedral or any other shape
 - d) Cyclohexane ----- Disc (b) or Disc (d)
 - e) p-dioxane ----- Disc or any shape.

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