Ultrasonic study of molecular interactions in some bio-liquids

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ABSTRACT

The velocity of ultrasonic wave of frequency 10 MHz has been measured by the ultrasonic Time Intervalometer using pulse echo overlap method, in the temperature range 10^0 to 55^0C, for the bio-liquids. Cinnamaldehyde, acrolein, acrylonitrile, methylmethacrylate, methanol, p-dioxane and cyclohexane. The relative strength of intermolecular interaction has been found to depend upon the presence of electron-donar and electron-accepter group. The ultrasonic parameters found useful in determining the relative strength of homo-molecular interaction in pure liquids.

Keywords: Ultrasonic velocity, compressibility, cinnamaldehyde, acrolein, methylmethacrylate, acrylonitrile, methanol, p-dioxane and cyclohexane.
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INTRODUCTION

The ultrasonic studies in bio-liquid are essential for utilizing them in bio-medical technology. Bio-liquids are made up of long chain molecules consisting of aromatic compounds. Bio-molecules are bigger in size and complicated in structure. The literature [1-3] shows scanty work on bio-liquids. Therefore it was though worthwhile to understand ultrasonic study on some bio-liquids. To understand the behavior of bio-molecules, representative, aliphatic, aromatic and α, β-unsaturated carboxyl compounds have been selected for study. The present paper explains the result of experimental and theoretical ultrasonic parameters of the bio-liquids cinnamaldehyde, acrolein, acrylonitrile, methylmethacrelate, methanol, p-dioxane and cyclohexane respectively. They are known to take active part in body metabolism. The methanol is a picular aliphatic

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alcohol with medicinal applications. It affects nerves system and causes total blindness, when taken in large amount. While p-dioxane & cyclohexane are aliphatic compounds. The cinnamaldehyale, acrolein, acrylonitril and methylmethacrelate are α, β-unsaturated carboxyl compounds and find applications in bio-medical technology and industries [4, 5]. To understand the behavior of α, β-unsaturated carboxyl compounds, namely cinnamaldehyde, acrolein, acrylonitrile and methylmethacrelate in the mixture with polar liquid methanol and non-polar liquids, p-dioxane and cyclohexane as a solvent were taken for experimental and theoretical ultrasonic studies in the present paper.

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, the liquids, cinnamaldehyde, acrolein, methylmethacrylate methanol and p-dioxane are oxygen bearing molecules, while cyclohexane is a cyclic compound with close ring.

Ultrasonic parameters are extensively being used to study molecular interactions in pure liquids [6], binary liquid mixtures [7-10] and ionic interactions in single and mixed salt solutions of bio-liquids [11,12]. The experimental investigations [13-16] have shown that derived parameters such as the adiabatic compressibility (β_a), the van der Waal's parameter (b), and their deviation from the additive rule provide a better insight into molecular processes. The present investigations was undertaken in order to study the dependence of the relative strength of intermolecular interactions and their nature in pure liquids on the constitution and environment of the molecule. The present paper describes the result of ultrasonic studies in a set of structurally related bio-liquids, such as cinnamaldehyde, acrolein, acrylonitrile, methylmethacrelate, methanol, p-dioxane and cyclohexane respectively. Though a few investigations are available in the literature, on some of the liquids studied here, no comprehensive ultrasonic study has yet been reported.

EXPERIMENTAL SECTION

The liquids used were BDH, Analar grade, redistilled in the laboratory before use. The velocity of ultrasonic wave of frequency 10 MHz was measured by the Ultrasonic Time Intervalometer, UTI-101 (Innovative instrument Hyderabad), using PEO technique in the temperature range 10-55^0C, for the pure liquids cinnamaldehyde, acrolein, acrylonitrile, methylmethacrylate, methanol, p-dioxane and cyclohexane and their mixtures.

The consistency of the oscillator frequency was checked, using a digital frequency meter and was found to be 4 in 10^4. The density of solution was measured by Hydrostatic sinker method in the temperature range 10-55^0C and had an accuracy of 1 in 10^4. The viscosity of the liquids was measured by Oswald's viscometer. The time of descent of the liquids between the viscometer marks was measured using designed electronic timer of very high accuracy. The temperature of the solution was maintained constant to 0.1^0C using an ultra thermostat U-10. The solution was stirred by moving the reflector and the sinker up and down. The data on the viscosity of water was taken from the literature [17]. The details of the experimental techniques were the same as reported earlier.

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The adiabatic compressibility, van der Waal's parameter b and viscosity η were obtained using standard relations [17, 18]. du/dT was obtained from velocity vs. temperature plots.

RESULTS AND DISCUSSION

The observed ultrasonic velocity (u), van der Waal's parameter (b), adiabatic compressibility (β_a) viscosity, (η), du/dT and other relevant parameters at 40^0C are given in table-1.

The value of van der Waal's volume parameter b for acrolein, acrylonitril, cyclohexane, p-dioxane and methanol are 58.865, 60.846, 98.042, 77.994 and 33.518 respectively (Table-1).. The addition of the CH_3 group thus the effective size of cyclohexane molecule from that of acrolein by nearly 39%. The addition of NH_2-group increases the effective size of p-dioxane molecule from that of acrylonitrile by nearly 17%. Due to resonance hybridization of acerolein or acrylonitrile in which the heteroatom (O, N) and the bond between C – N/O, attains a definite double bond character. As the double bond involves SP^2, hybridization [14], it has necessarily to be float. On the other hand methyl addition involves the Sp^3 tetrahedral arrangement. Thus the effective size of the molecule will increase due to the three dimensional methyl group.

Table-1: Ultrasonic and some relevant parameters for pure liquids at 40^0C

Sr. no	Liquids	Molecular weight in (gm)	Density (gm CC^{-1})	Viscosity (CP)	v.d.w b (cm^3 mole$^{-1)}$)	Ultrasonic velocity (msec$^{-1)}$)	Compressibility β_a x 10^{-9} (m^{2}dyne$^{-1)}$)	du/dT
1	Cinnamaldehyde	132.16	0.9698	0.1394	126.773	1339.75	0.57	-3.510
2	Acrolein	56.06	0.8263	0.2266	58.865	1134.11	0.94	-3.997
3	Acrylonitrile	53.06	0.7770	0.2032	60.846	1385.00	0.67	-4.000
4	Methylmethacrelate	100.12	0.9946	0.0650	90.799	1114.96	0.08	-2.497
5	Methanol	32.04	0.7650	0.2971	33.518	1054.40	1.17	-3.140
6	Cyclohexane	84.16	0.7640	0.4766	98.042	1196.00	0.91	-4.400
7	p-dioxane	88.11	1.033	0.6112	77.994	1310.00	0.07	-4.242

The slightly different values of 'b' amongst the cyclohexane or p-dioxane may be taken as an indication of an intramolecular interaction between the methyl and hydroxyl group, in p-dioxane. The observed large increase in the value of 'b' cinnamalelehycle (126.773) and methylmethacrylate (90.799) with that of acrylonitrile (60.846) is due to the addition of CH_3-or OH group.

The decrease velocity in acrolein compare with that in p-dioxane can be understood from the observed large increase in compressibility. This increase shows a tendency towards ordering, resulting in a decrease in ultrasonic velocity.

The observed decrease in du/dT seems to be associated with the ordering tendency. The OH$^-$ group, being an electron accepter, decreases the election density. The ordering tendency in acrolein is due to the hydrogen bonds which is the OH$^-$ group can form.

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Acrylonitrile:

The change of molecular volume relative to p-dioxane is nearly 17%, due to the addition of CH_3 group. The compressibility increases from 0.67 to 0.07 x 10^{-9} m^2 $dyne^{-1}$. This shows a slight decrease in the ordering taking place in acrylonitrile. The observed increase in the velocity and increase in du/dT is thus associated with ordering. The CH_3 group, being an electron donor decreases the electron density. In the acrylonitrile the closeness of du/dT values in acrylonitrile and p-dioxane shows that the electron density in acrylonitrile and p-dioxane may not differ markedly.

Cinnamaldehyde:

The larger molecular weight of cinnamaldehyde and their lesser density, compare to that of p-dioxane shows an increase in volume. The increase in b is of the same order as that of p-dioxane. This change in volume thus dominated by CH_3 group. However the values of velocity and du/dT are close to those of p-dioxane.
This indicates the dominance of the OH^- group in cinnamaldehyde-cinnamaldehyde interaction.

Methyl methacrylate:

The change of molecular volume, relative to methanol in nearly 57%, due to the addition of CH_3 group. The compressibility decreases from 0.08 to 1.17 x 10^{-9} m^2 $dyne^{-1}$. This shows increase in the ordering taking place in methylmethacylate. The observed increase in velocity is thus associated with ordering. The CH_3 group being an electron donar increases the electron density in methylmethacrylate and methanol may not differ markedly.

CONCLUSION

The relative strength of intermolecular interaction has been found to depend upon the presence of electron-donar and electron-accepter group. The ultrasonic parameters found useful in determining the relative strength of homo-molecular interaction in pure liquids.

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