Study of positional isomerism in N-propyl and Iso-propyl alcohol using ultrasonic technique

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Abstract. In the present work, positional Isomerism is studied in the binary mixtures of n-propyl alcohol and Iso-propyl alcohol in nitrobenzene as the common solvent. Ultrasonic velocity and attenuation measurements using pulse–echo technique operated at 10 MHz have been taken at various concentrations of both alcohols in nitrobenzene, from 283.15K - 293.15K. It is observed that both the systems exhibit critical nature and show non-linear variation both in ultrasonic velocity of propagation and attenuation. Ultrasonic attenuation at lower concentrations of n-propyl alcohol in nitrobenzene reveals the dominant structural relaxation as compared to that of Iso-propyl alcohol in nitrobenzene.

Keywords. Ultrasonic pulse echo technique, ultrasonic velocity and attenuation, positional Isomerism, molecular interaction, dispersive forces.

1. Introduction

Binary mixtures formed by different liquids can be homogeneous or heterogeneous. Such mixtures result in change of physical and chemical properties that can be studied in the light of closely observing molecular interactions, dispersive forces, hydrogen bonding or dipole-dipole interactions. Various techniques viz, NMR, IR, optical spectroscopy, ultraviolet, visible spectral methods etc. unfold many properties of mixtures. Ultrasonic measurements are very effective, sufficiently sensitive and reliable to study the molecular interactions in liquids as ultrasonic evaluations throws light on inter and intra molecular interactions [1-7]. Several workers have reported work on the ultrasonic propagation velocity in alcohols using ultrasonic interferometer [8-11]. On the other hand, ultrasonic attenuation is sensitive to the chemical composition of the mixture [11].

N-Propyl alcohol and Iso-propyl alcohol belong to the same family of alcohols but have different molecular structures and exhibit different properties [12]. In the present work, ultrasonic parameters like velocity and attenuation are measured in mixtures of n-propyl and Iso-propyl alcohols in nitrobenzene at 10 MHz pulse echo technique.
2. Experimental

2.1 Materials

N-propyl alcohol, Iso-propyl alcohol and Nitrobenzene (AR Grade Merck) are used for the preparation of mixtures, without further filtration or distillation. Double distilled water is used to calibrate the cell. Design of sample holder is of utmost importance and critical for accurate measurements. For highly attenuating liquids path length is chosen to lie in Fresnel’s zone i.e., less than the near field zone. Also, the cell contains internal grooves which removes the internal reflections, inner walls should be non-corrosive so made up of stainless steel. Parallelism issue is removed by properly adjusting the transducer with the bottom of the cell. Bottom of the cell is mirror finished. Two-fold cylinder is used for maintaining the constant temperature of the sample. Freshly prepared mixtures are used at the time of measurements.

2.2 Method

Velocity and attenuation measurements for both the mixtures are carried out by pulse echo technique functioned at 10 MHz. This system is designed in our lab, by using a Kalman Filter. This linear Kalman Filter is helpful to extract signals from the noise. In this technique, ultrasonic waves are generated by bombarding a voltage of 52V, which excites the piezoelectric transducer. (PZT) This (PZT) transducer is disc of diameter 10 mm (Concord Transducer and Instrument Co., New Delhi, India) with a wraparound solder arrangement. A high voltage pulse arrester is kept at the receiver section and amplified signal is then fed to Digital Storage Oscilloscope (DSO) (Tektronix TDS 2014). Ultrasonic velocity is calculated using time of flight (ToF) for two consecutive echoes over a fixed path length measured during calibration and then taking average values of them measured on DSO. Kalman filter plays an important role for measurement of velocity Use of Kalman Filter reduces the variations in the measurement due to sudden temperature changes, noise [13] etc.

Relaxation phenomenon can be studied for various frequencies. Due to the lack of such type of system, readings are noted at 10 MHz.

![Figure 1. Schematic diagram, for Pulse Echo system](image)
\[ u = \frac{2d}{t} \]  \quad \text{(1)}

Where, \( u \) = ultrasonic velocity  
\( d \) = path length of the sample  
\( t \) = time of flight

For maintaining constant temperature, Thermostat (Julabo F32) with an accuracy of ±0.1°C is used. The amplitudes of successive echoes are measured from DSO and attenuation is calculated as shown

\[ \alpha = \left(\frac{20}{2d}\right) \log_{10} \left(\frac{A}{A_0}\right) \]  \quad \text{(2)}

DSO has limited window resolution, this limits accuracy in the measurement. So, amplitude measurement can be done for three consecutive echoes.

3. Results and Discussion

![Propyl alcohol (1-propanol)](image1.png)  
![Isopropyl alcohol (2-propanol)](image2.png)

**Figure 2.** Molecular Structure of n-propyl and Iso-propyl alcohol

![Graph](image3.png)

**Figure 3.** Variation of ultrasonic velocities in n-propyl and Iso-propyl alcohol in a nitrobenzene mixture with concentration at 279 K and 281 K respectively
Figure 4. Variation of ultrasonic velocities in n-propyl and Iso-propyl alcohol in a nitrobenzene mixture with temperature at 0.58 M and 0.67 M concentration respectively.

Figure 5. Variation of ultrasonic attenuation in n-propyl and Iso-propyl alcohol in a mixture with Nitrobenzene.
Behavioural trends in ultrasonic velocity and attenuation measurements in the mixtures of n-propyl alcohol and Iso-propyl alcohol in common solvent, nitrobenzene, are compared in order to study the Isomerism.

Isomerism is a phenomenon in organic chemistry where the materials have the same molecular formula with same number of atoms in a molecule but different structural or spatial arrangement within the molecule. There are two basic types of isomerism viz. Structural isomerism and stereo-isomerism. Structural Isomerism are further subdivided as Chain Isomerism (2) Positional Isomerism and (3) Functional Isomerism. Stereo-isomerism is subdivided as (1) Geometric Isomerism and (2) Optical Isomerism

In the present paper, an attempt is being made to study the positional isomerism in N-propyl and Iso-propyl Alcohol. This is the first pair of isomers. In positional isomerism, functional group is attached to different carbon atoms in a chain which changes the reactivity of that material. Mixtures of two alcohols are studied for isomerism and the results are as follows.

Figure 3 shows the variation of ultrasonic velocity Vs. Concentration. Pure Nitrobenzene is showing the highest velocity. The velocity of propagation is observed to decrease with increase in concentrations of both the alcohols in nitrobenzene. This is due to the polar nature of the alcohols, with hydroxyl group that exhibit self-associative nature. This results out of the lower density of Iso-propyl [14]. Mixing of associated and non-associated liquids leads to dipole-induced interactions. Figure 4 shows that as temperature increases ultrasonic velocity decreases since increasing temperature weakens the molecular forces. In N-propyl Alcohol, O-H is attached to a primary carbon atom. So, it is called Primary alcohol. Whereas in Isopropyl alcohol, O-H group [15-16] is shifted from terminal carbon to secondary carbon, so called as secondary alcohol. (Figure 2). Hydrogen Bonding is an interaction among hydrogen, oxygen, or nitrogen. A strong dipole-dipole interaction is generally called hydrogen bonding. Large partial positive charge on hydrogen atom and large partial negative charge on oxygen or nitrogen atom, there is large difference in the electro-negativity. In primary alcohol as the functional group O-H is attached to an open-ended carbon atom, electronegative oxygen atom will show dipole-dipole interaction with nitrobenzene solvent, whereas, when molecules of secondary alcohol interact with nitrobenzene, it shows induced- dipole force to be active. With rise in temperature these forces get weaker [17-26].
Figure 5 shows variation of ultrasonic attenuation in alcohols-nitrobenzene mixtures. In the present work, we have taken measurements at temperature of 279.15 K for n-propyl alcohol and 281.15 K for Iso-propyl alcohol as, we have observed maxima at these temperatures. The mixture of nitrobenzene and alcohol shows maxima for an intermediate concentration viz., N-type and nitrobenzene maxima is observed for 0.58M and Iso-type and nitrobenzene at 0.67M concentration. As polar alcohol is added in non-polar nitrobenzene, there is a structural change in the linear chain of alcohols. Attenuation at lower concentration in primary alcohol shows, structural relaxation is dominant in it than that is observed in Iso-propyl alcohol. Fig. 6 shows the variation of ultrasonic attenuation with temperature at 0.58 M of primary alcohol and 0.67 M of secondary alcohol. N-propyl alcohol shows ultrasonic attenuation at lower temperature than that of Iso-propyl alcohol as it has less packing ring structure due to hydrogen bridges as shown in Fig 2. In Fig 4 (b), there can be two independent peaks due to the complex formation between two distinct molecules in two different ways, as like [27].

4. Conclusion

Positional Isomerism is studied for the N-propyl and Iso-propyl in nitrobenzene as a solvent. Isomerism can be identified firstly from the O-H group, which is attached to first carbon in N-propyl and to second carbon in Iso-propyl. Secondly, ability of carbon chains linking together, thirdly stability of bond formation with elements such as oxygen, nitrogen, hydrogen, etc. Following results were found after studying the mixtures of both alcohols with nitrobenzene.

Ultrasonic velocity measurement reveals dipole-dipole and dipole-induced dipole interactions among the polar components in the mixture of alcohols and nitrobenzene. With increase in temperature intermolecular forces get weaker leading to the decrease in ultrasonic velocity.

Ultrasonic absorption in un-associated liquids is observed due to the alteration of alcohol structure due to concentration fluctuation and the interaction between unlike molecules in a mixture having one of the components being highly attenuating. The absorption peaks decrease with the increase in temperature which is the dissipative phenomenon due to thermal agitation. As the two temperature peaks are observed for two different temperatures, these are called upper and lower phase. This peak is observed for N-propyl + Nitrobenzene at 0.57 M and temperature at 279 K and for iso-propyl + Nitrobenzene at 0.67 M and temperature 281 K. The absorption is increasing at these phases when the solution temperature is approaching rapidly. Higher attenuation, at lower temperature of N-propyl alcohol as compared to that observed in Iso-propyl alcohol, reveals the difference in the behaviour of two isomers.

5. References

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6. Acknowledgement

The authors are thankful to Prof. O. P. Chimankar, Head of the Department of Physics, Rashtrasanta Tukadoji Maharaj Nagpur University, Nagpur, for providing the necessary facilities to carry out the work. One of the authors (RT) is thankful to Mr. Sanjiv Dubey for assisting in the experimental work and to the Director, G H Raisoni College of Engineering for kind support.