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Study of Acoustical Parameters of a Cholesteric Liquid Crystal and Toluene Solutions

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Acoustical parameters are the best tool to understand the molecular interaction of a solution of Cholesteric liquid crystal (CLC) and Toluene solvent. Acoustic Impedance (A), Adiabatic Compressibility (β_a), Rao's Constant (R), Wada Constant (W) & Viscous relaxation time (τ) of the solutions with varying Mole Fraction of Cholesteryl Acetate using an ultrasonic interferometer and Ostwald's viscometer. The measurements were made using an Ultrasonic interferometer at 1 MHz frequency at room temperature. It has been established that moderate molecular interactions are present in the systems.

Keywords: Acoustical parameters, Cholesteric liquid crystal, Cholesteryl acetate, Toluene, Ultrasonic interferometer

1 Introduction

Ultrasonic studies of cholesteryl acetate are limited; however, related research on cholesteric liquid crystals and cholesterol derivatives provides insights into its potential behavior. Studies on cholesteryl derivatives like cholesteryl stearate, laurate, and propionate have shown that ultrasonic absorption and velocity exhibit significant changes near the isotropic-cholesteric transition temperature. These changes are attributed to structural relaxations and phase transitions within the liquid crystalline phases[1]. Polymer-Dispersed Liquid Crystal (PDLC) composites based on chitosan and cholesteryl acetate were studied[2]. The ability of chitosan to act as a polymeric matrix for the encapsulation of cholesteryl acetate liquid crystal to obtain eco-friendly PDLC composites is demonstrated. Fourier Transform Infrared Spectroscopy (FTIR), RAMAN spectroscopy, and Polarized Optical Microscopy (POM) are used for the study of PDCLC. The absorption and dispersion of ultrasound in three cholesteryl esters and their mixtures were studied using a pulse transmission technique[3]. The thermal behaviour of cholesteryl acetate was studied using thermal analytic microscopy (microscopy synchronized with thermal analysis) and X-ray powder diffraction[4]. It is established that Cholesteryl acetate crystallized from 1-pentanol has two forms, "A" and *"C"*. ''A" is stable at room temperature, and "C" is stable above 85 °C. Various solid polymorphs formed by fusion belong to the *"C"* form. Absence of impurities helps to form "A". Acoustical parameters are still not studied for Cholesteryl Acetate (CA) and Toluene mixture. Which is important to understand molecular interactions and structural behaviour of Cholesteryl Acetate (CA).

A systematic ultrasonic investigation of the cholesteryl acetate–toluene binary system was studied for the first time. Unlike previous studies on cholesteric esters and polymer-dispersed systems, the present work provides a comprehensive multi-parameter acoustical and thermodynamic analysis, revealing non-monotonic behaviour in Rao's and Wada's constants and indicating concentration-dependent structural reorganization. The results establish baseline acoustic data and offer new insight into molecular interactions in cholesteric liquid crystal solutions.

The Wada constant, Rao's constant, Adiabatic compressibility, and viscosity of the solution were determined by varying the concentration of the solution. Ultrasonic velocities for the solutions of different concentrations were measured. The ultrasonic interferometer (Mittal Enterprises, India; Model: F-80X) was used for the measurements of the velocity of ultrasonic waves in the solvent and solution. It consists of a high-frequency generator and

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a measuring cell, and the measurements were made at 1 MHz. The least count of the micrometer measuring cell is 0.01mm. The ultrasonic velocity has an accuracy of ± 0.5 %. It is used to find the Acoustic Impedance, Rao's constant, Adiabatic Compressibility, and Wada constant. The viscosity was measured by Oswald's viscometer. It is used to find Van der Waals' constant, Free Volume, Internal pressure, and Classical Absorption Coefficient of the five samples prepared in the laboratory. An ultrasonic interferometer was used to find the ultrasonic velocity at 1MHz frequencies at room temperature, and Ostwald's viscometer was used to find the viscosity of the liquid crystal.

Using ultrasonic velocity and viscosity, the physical and chemical parameters of the Cholesteric liquid crystal (CLC) solutions were obtained. These parameters lead to understanding the chemical as well as physical properties of liquids and their interactions.

2 Materials and Methods

The samples were prepared using Cholesteryl Acetate (CA), a CLC having molecular formula $C_{29}H_{48}O_2$ and molecular weight of 0.4287 Kg/mol, as obtained from Sigma, Aldrich is used in the preparation of the samples. The neutral solvent Toluene, having molecular formula C_7H_8 and molecular weight of 0.09214 Kg/mol, was used to prepare the solution of various concentrations. Different solutions having CA mole fractions 0.02, 0.04, 0.06, 0.08, and 0.1 in Toluene solvent were prepared.

The velocity of sound in solutions was studied using an ultrasonic interferometer Model: F-80X procured from Mittal Enterprises, India. Further, following constants, namely Acoustic Impedance (A), Adiabatic Compressibility (β_a), Rao's Constant (R), Wada Constant (W) & Viscous relaxation time (τ) are computed[5–8]. The formulas for these constants are provided below.

2.1 Theoretical calculations

The density, viscosity, and ultrasonic velocity have been calculated with the experimental data using standard formulas.

i Acoustic Impedance (A) is determined by the standard equation

$$\text{Acoustic Impedance (A)} = U\rho \text{ Kg/m}^2\text{.sec} \quad \dots (1)$$

where U is ultrasonic velocity, and ρ is density

ii Rao's constant (R) is calculated by the standard formula

$$\text{Rao's constant (R)} = \frac{M_{eff}}{\rho} U^{\frac{1}{3}} (m^3/mole)\,(m/s)^{-\frac{1}{3}} \quad \dots (2)$$

where, $Effective\ Mass\ M_{eff} = \sum_i M_i x_i$ (M_i Molecular weights and x_i Mole fractions. The mole fraction can be calculated from the masses m_i and molar masses M_i (kg/mol) of the components:

$$x_i = \frac{\frac{m_i}{M_i}}{\sum_i \frac{m_i}{M_i}} \quad \dots (2a)$$

iii Adiabatic Compressibility (β_a): The ultrasonic velocity in a liquid medium is determined by the bulk modulus and density of the medium using the Newton-Laplace equation

$$(\beta_a) = \frac{1}{U^2 \rho} \ Pa^{-1} \quad \dots (3)$$

iv Wada Constant (W) is calculated with the standard equation

$$(W) = \frac{M_{eff}}{\rho} \beta_a^{-\frac{1}{7}} \ (m^3/mole)\,(Pa^{-\frac{1}{7}}) \quad \dots (4)$$

where, M_{eff} is Effective Mass, ρ is density & β_a is Adiabatic Compressibility.

v Viscous relaxation time (τ) is calculated by using the standard equation

$$(\tau) = \frac{4\eta}{3\rho U^2} \text{ sec} \quad \dots (5)$$

where, η, ρ & U are viscosity, density & ultrasonic velocity of the solution.

vi Free Volume (Vf) is calculated by the standard formula

$$(V_f) = \left[\frac{M_{eff}\, U}{K\eta}\right]^{3/2} \text{ m}^3 \text{ mol}^{-1} \quad \dots (6)$$

where, M_{eff} is Effective Mass, η is viscosity, U is ultrasonic velocity of solution & K is a temperature-independent constant which is 4.28×10^9 in the MKS system for all liquids.

The Velocity (U) measured using an ultrasonic interferometer, Density (ρ), and Viscosity (η) of all samples are provided in Table 1. Acoustical parameters of all samples were calculated using Equations 1, 3, and 5 and provided in Table 2. Thermodynamic parameters for all samples were

Table 1 — Velocity (U), Density (ρ), and Viscosity (η) of samples

Mole Fraction of CA	Ultrasonic Velocity U (m/s)	Density ρ Kg/m^3	Viscosity η x10^{-3} (N.s/m^2)
0	1292	870	1.202
0.02	1304	952.6	1.624
0.04	1312	1038.7	1.908
0.06	1316	1128.4	2.437
0.08	1332	1173.4	2.951
0.1	1336	1271.2	4.226

Table 2 — Acoustical parameters of samples

Mole Fraction of CA	Adiabatic compressibility β_a (pa^{-1})	Acoustic impedance A (kg $m^{-2}s^{-1}$)	Viscous relaxation time τ (s)
0	6.88582E-10	1124040	1.1036E-12
0.02	6.17354E-10	1242190.4	1.33658E-12
0.04	5.59297E-10	1362774.4	1.42284E-12
0.06	5.11711E-10	1484974.4	1.66281E-12
0.08	4.80336E-10	1562968.8	1.88964E-12
0.1	4.40731E-10	1698323.2	2.48337E-12

Table 3 — Thermodynamic parameters of samples

Mole fraction of CA	Free volume V_f (m^3/mole)	Rao's constant R (m^3/mole)(m/s)$^{1/3}$	Wada's Constant W (m^3/mole)(Pa)$^{-1/7}$
0	1.11308E-07	0.0011535	0.002156713
0.02	7.99046E-08	0.0011339	0.002146828
0.04	6.98848E-08	0.001113	0.002132795
0.06	5.33536E-08	0.0010909	0.002115089
0.08	4.45064E-08	0.0011164	0.00217543
0.1	2.83237E-08	0.0010899	0.002147829

calculated using Eqs. (2), (4), and (6) and provided in Table 3.

3 Results and Discussion

Adiabatic Compressibility (β_a), Acoustic Impedance (A), Viscous relaxation time (τ), Classical Absorption Co-efficient, Free Volume (V_f), Rao's constant (R), Wada Constant (W) of CLC solution were determined with varying Molar Fraction.

The plot of ultrasonic velocity (U) versus mole fraction of cholesteryl acetate (CA) (Fig. 1) depicts a significant increase in U with the initial addition of CA. This suggests enhanced molecular packing and moderate intermolecular interactions between CA and toluene molecules. As CA concentration increases further, the rate at which ultrasonic velocity increases slows down, depicting structural reorganization within the solution. Similar behaviour has been reported in ultrasonic studies of cholesteric liquid crystals, where initial solute addition leads to stronger associative interactions, followed by stabilization or restructuring at higher concentrations[9].

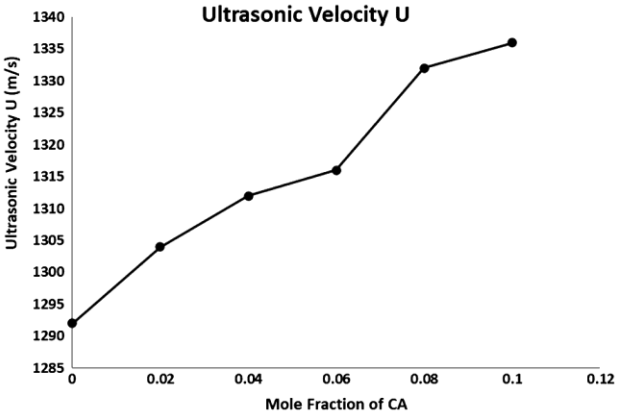

Fig. 1 — Ultrasonic Velocity (U) vs Mole Fraction of CA

The plot of viscosity versus mole fraction of cholesteryl acetate (CA) (Fig. 2) exhibits that initial addition of CA leads to a significant increase in viscosity, indicating its strong influence on the solution's viscous behaviour. As the mole fraction of CA increases further, the viscosity rises more rapidly, suggesting that intermolecular interactions become increasingly pronounced at higher concentrations. This trend is consistent with previous studies on liquid crystal solutions, where higher concentrations of solutes lead to enhanced molecular interactions and increased resistance to flow[10,11].

The plot of adiabatic compressibility versus mole fraction of cholesteryl acetate (CA) (Fig. 3) depicts a significant decrease in compressibility with an

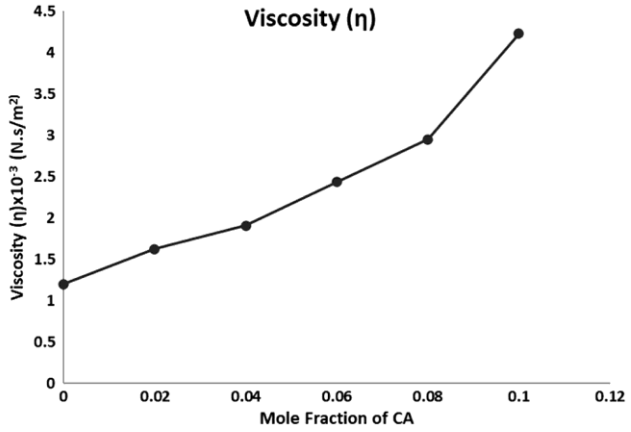

Fig. 2 — Viscosity (η) vs Mole Fraction of CA

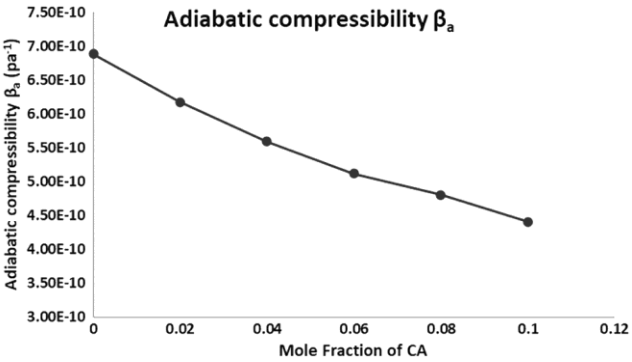

Fig. 3 — Adiabatic compressibility β_a (pa^{-1}) vs Mole Fraction of CA

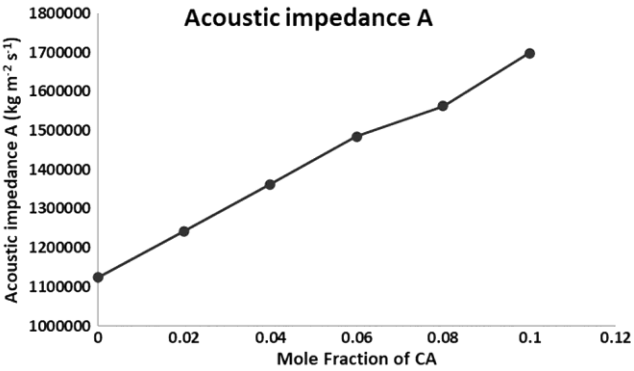

Fig. 4 — Acoustic impedance A (kg $m^{-2}sec^{-1}$) vs Mole Fraction of CA

increase in CA concentration. This indicates that CA strongly influences the solution's compressibility, with higher mole fractions leading to progressively lower adiabatic compressibility[10,11].

The plot of acoustic impedance versus mole fraction of cholesteryl acetate (CA) (Fig. 4) exhibits a linear increase in acoustic impedance with an increase in CA concentration. The addition of CA enhances the

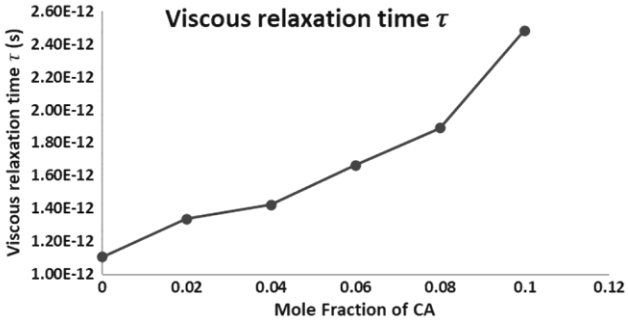

Fig. 5 — Viscous relaxation time (τ) (sec) vs Mole Fraction of CA

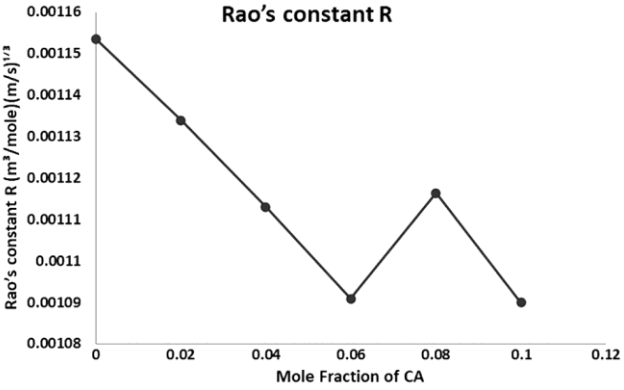

Fig. 6 — Rao's constant (R) vs Mole Fraction of CA

solution's acoustic impedance, due to increased density and sound velocity resulting from moderately molecular interactions and tighter molecular packing. This behaviour corroborates the results reported in the binary system[12].

The plot of viscous relaxation time versus mole fraction of cholesteryl acetate (CA) (Fig. 5) shows a significant increase in viscous relaxation time with the addition of CA. This depicts that CA has a substantial effect on the solution's ability to return to equilibrium after being disturbed. The increase in viscous relaxation time indicates that CA moderately influences the solution's molecular interactions, which slows down the system's relaxation process, particularly at higher concentrations. As the mole fraction of CA rises, these interactions become more pronounced, leading to a greater resistance to molecular movement and, consequently, a longer viscous relaxation time.

The plot of Rao's constant versus mole fraction of cholesteryl acetate (CA) (Fig. 6) shows that the relationship between Rao's constant and the mole fraction of CA is non-monotonic. It initially decreases, then increases, and finally decreases again.

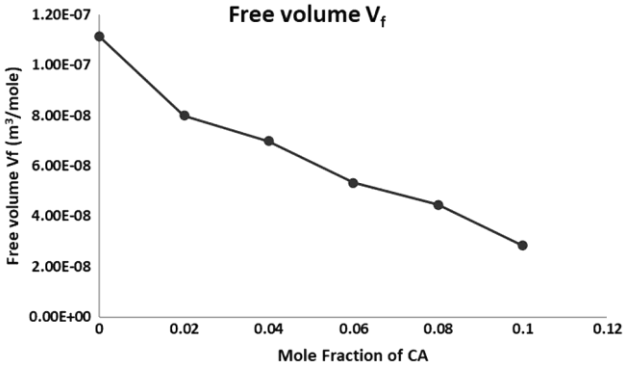

Fig. 7 — Free volume (V_f) vs Mole Fraction of CA

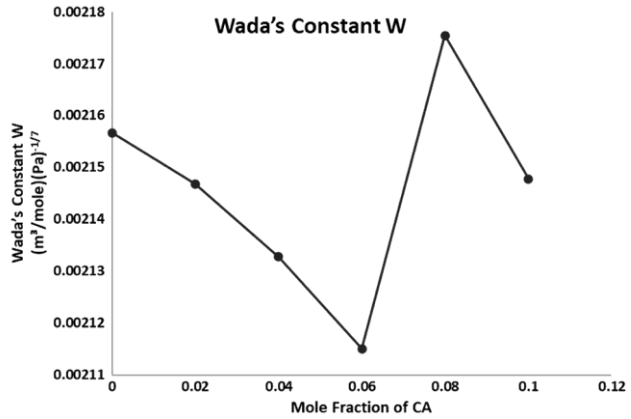

Fig. 8 — Wada's Constant (W) vs Mole Fraction of CA

This suggests a complex interplay of factors influencing Rao's constant.

Rao's constant reaches a minimum at an intermediate mole fraction of CA. This indicates that the molecular packing and size are most compact at this particular concentration. The relationship is nonlinear, suggesting that the factors influencing Rao's constant are not linearly related to the mole fraction of CA[13].

The plot of free volume versus mole fraction of cholesteryl acetate (CA) (Fig. 7) shows that initial addition of CA leads to a significant decrease in free volume. This suggests that CA has a strong influence on the available free volume at low concentrations[14]. As the mole fraction of CA continues to increase, the rate at which free volume decreases slows down. This indicates that the effect of adding CA becomes less pronounced at higher concentrations.

Figure 8 depicts Wada's constant as a function of the mole fraction of CA. With an initial increase in CA percentage up to x = 0.06, Wada's constant decreases. Wada's constant exhibits interaction between molecules of a material, and hence imperative that molecular interactions decrease for the initial increase in CA. This indicates that the molecular packing and size are most compact at this particular concentration[15]. Further, for x = 0.08 CA, an increase in Wada's constant depicts enhanced interactions due to the formation of a complex structure. Thereafter, a small decrease in Wada's constant is observed for higher concentrations of CA.

The approach of tuning material properties will be helpful to develop new materials for Actuators[16], Sensors and photonic devices[17,18].

4 Conclusion

The acoustic parameters of a Cholesteric Liquid Crystal and Toluene solutions are thoroughly investigated in the present work. The addition of CA enhances ultrasonic velocity, reduces adiabatic compressibility, and increases viscosity and acoustic impedance, depicting moderate molecular interactions and improved packing, suggesting structural reorganization. Rao's constant(R) and Wada's Constant (W) exhibit nonlinearity. The change in Rao's and Wada's constants with an increase in CA depicts a change in molecular interactions. The change in Wada's constant and Rao's constant corroborate with each other.

The results of this study provide valuable insights into the behaviour of cholesteryl acetate CA in toluene, particularly regarding its influence on the solution's acoustic, thermodynamic, and structural properties. The observed behaviour affirms the sensitivity of ultrasonic parameters to subtle molecular interactions in liquid crystal solutions and suggests potential for tuning solution properties through controlled variation of CA concentration.

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