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Ultrasonic Investigation of the Effects of Concentration and Temperature on Ferulic Acid–Polyethylene Glycol Interactions

Smita S. Kharkale-Bhuyar

Assistant Professor, Department of Chemistry

Shri Lemdeo Patil Mahavidyalaya, Mandhal, Kuhi, Nagpur, Maharashtra, India.

Corresponding Author - Smita S. Kharkale-Bhuyar

Abstract: *Higher concentrations of PEG lead to enhanced molecular interactions, as evidenced by increased acoustic impedance and decreased adiabatic compressibility and intermolecular free length. To assess key acoustic properties—namely acoustic impedance (Z), adiabatic compressibility (β), intermolecular free length (Lf), relaxation time, and Gibbs free energy—the experimental parameters of density (ρ), viscosity (η), and ultrasonic velocity (U) were employed. As temperature rises, these molecular interactions weaken, resulting in a decline in acoustic impedance and shifts in thermodynamic behavior, including an increase in Gibbs free energy*

Keywords: Ultrasonic Velocities, Isentropic Compressibility, Intermolecular Free Length, Specific Acoustic Impedance and Thermo-Acoustic Parameters

I. INTRODUCTION

The physicochemical properties of liquid mixtures, such as density (ρ) and viscosity (η), are fundamentally governed by their intermolecular forces. An understanding of these properties is vital for applications in chemical separations, solvent theory, heat transfer, and molecular mechanics Consequently, the systematic study of molecular interactions in liquid systems, both theoretically and experimentally, has become standard practice [1–3].

Ultrasonic technology has emerged as an invaluable, non-destructive tool for probing the molecular behaviour and structural characteristics of pure and mixed liquids [3–4]. Measurements of density, viscosity, and ultrasonic velocity (U) allow researchers to calculate various acoustical parameters and identify the presence of both stronger and weaker molecular interactions in binary and ternary liquid mixtures. The velocity of sound, being a key physical characteristic, helps in comprehending the liquid state.

The study of molecular interactions in polymer solutions is of significant interest, particularly for the engineering applications of polymers [5–8]. Polyethylene glycol (PEG-600) is a high-molecular-weight polymer extensively used in pharmaceuticals, coatings, and materials science due to its biocompatibility and solubility. Its simple structure, featuring etheric and hydrogen linkages, makes it an excellent candidate for studying structural effects, as it can form hydrogen bonds with solvents like Ferulic Acid [9–10].

When PEG-600 is dissolved in ethanol, the intricate molecular interactions significantly influence the solution's physical properties, including viscosity, density, and acoustic behaviour. Understanding these interactions is crucial for optimizing PEG-based formulations in various industrial and scientific fields [11–13].

Aims and Methodology of the Study

This investigation utilizes ultrasonic techniques to explore the molecular interactions between PEG and Ferulic Acid. By measuring ultrasonic velocity, density, and viscosity, researchers can calculate key thermo-acoustic characteristics, such as: Acoustic Impedance (Z), Adiabatic Compressibility (β), Intermolecular Free Length (Lf), Relaxation Time (Ʈ), Gibbs Free Energy (ΔG). These parameters provide valuable insights into the underlying molecular dynamics, the strength and nature of molecular associations, and any resulting structural rearrangements within the system [14-16].

The study specifically examines the PEG- Ferulic Acid system by systematically varying, Concentration are 5%, 10%, and 15%, Temperatures: 298K, 308K, 318K, and 328K with Constant Frequency: 4-MHz. While other methods like spectroscopy, calorimetry, and rheology offer useful details, ultrasonic techniques provide a unique combination of advantages: Non-destructive: The technique does not alter the sample, allowing for repeated and stable measurements. Sensitive and Versatile: It captures instantaneous molecular interactions without degrading the sample. Dynamic Insight: It enables the real-time monitoring of molecular interactions as a function of time, temperature, or concentration, providing dynamic information difficult to obtain otherwise. The detailed analysis of the aforementioned acoustic and physical parameters is expected to yield a comprehensive understanding of the molecular dynamics within the PEG- Ferulic Acid system, contributing valuable knowledge to fields like material science, biophysics, and chemical engineering [17-18].

II. MATERIALS AND METHODS

This study investigated the molecular interactions in solutions of Polyethylene Glycol (PEG) and Ferulic Acid. Preparation: Analytical Reagent (AR) grade PEG and Ferulic Acid were sourced from E-Merk Ltd. (India). Solutions: Three solutions were prepared by weight using PEG in Ferulic Acid: 5%, 10, 15%.

Experimental Measurements: The experiments focused on measuring density (ρ), viscosity (η), and ultrasonic velocity (U) as a function of PEG concentration across a range of temperatures. Temperature Range: 298K, 308K, 318K, and 328K (equivalent to 25^0C, 35^0C, 45^0C and 55^0C) at 4 MHz in frequency an ultrasonic interferometer was used to detect ultrasonic velocity (Model M-84, supplied by M/S Mittal Enterprises, New Delhi) considering the precision of ±0.1 m s-1. Temperature Control: A digital constant temperature bath (Model SSI-03 Spl, M/S Mittal Enterprises, New Delhi) was used. It maintains a temperature range from 10^0C to 85^0C with a precision of $\pm 0.1^0$C. The bath circulates water through the outer jacket of the measurement cell, which is double-walled and contains the experimental liquid. The viscosity was measured using an Oswald viscometer (10 mL) with an accuracy of ±0.001 Ns m-2. Using an ac curate digital racer stopwatch, the flow time was ascertained of ±0.1 s. These parameters are calculated by using standard relations [18-19].

Theoretical Aspect

Using the experimental data for density (ρ), viscosity (η), and ultrasonic velocity (U), several **thermo-acoustic parameters** were calculated using standard formulas. These parameters provide deeper insight into molecular dynamics and interactions within the solution.

Acoustic Impedance (Z): A measure of the resistance the medium offers to the propagation of sound waves:

$$Z = \rho\, U \ (kg.m^2.s^{-1}) \qquad (1)$$

Adiabatic Compressibility (β): Determined by the Newton-Laplace equation, it measures the liquid's relative volume change under pressure at a constant entropy

$$\beta = \frac{1}{\rho\, U2}\ (N^{-1}\ m^2) \qquad (2)$$

Intermolecular Free Length (Lf): This parameter, based on Jacobson's conventional expression, relates to the distance between the surfaces of neighbouring molecules.

$$Lf = \frac{K_T}{U\rho^{1/2}}\ (N^{-1}\ m^2) \qquad (3)$$

Where K_T is Jacobson's constant, which varies with temperature: $K_T = (93.875 + 0.375\ T)\ x10^{-8}$

Viscous Relaxation Time (Ʈ): This parameter relates to the time required for a liquid to recover its equilibrium state after a pressure perturbation.

$$Ʈ = 4/3\ (\beta.\eta)\ (s) \qquad (4)$$

Gibb's Free Energy (ΔG): Calculated by applying the Eyring salt process theory to the temperature fluctuation of the relaxation time (Ʈ):.

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$$\Delta G = 2.30KT \log \frac{kT\tau}{h} \, (KJ.mol) - 1 \quad (5)$$

where "T" is the absolute temperature, "k" is the Boltzmann constant, h is the Planck constant.

III. RESULTS AND DISCUSSION

The observed variations in experimental and acoustic parameters of PEG + Ferulic Acid solutions across different concentrations and temperatures can be interpreted through molecular interactions. These interactions are predominantly governed by hydrogen bonding, van der Waals forces, and the inherent structural characteristics of PEG.

Solutions of PEG in Ferulic Acid were studied at concentrations ranging from 5% to 15% and temperatures of 298K, 308K, 318K, and 328K. Measurements of density and viscosity under these conditions were used to calculate several thermodynamic and acoustic properties, including ultrasonic velocity (U) and acoustic impedance (Z), as presented in Tables 1–2.

Density increase in PEG concentration leads to a noticeable rise in solution density. This is due to the addition of PEG molecules, which have a higher molecular weight than Ferulic Acid, resulting in greater mass per unit volume. The denser molecular packing further contributes to this increase Conversely, as temperature increases, the density tends to decrease (Fig.1) [20-22].

Viscosity rises with increasing PEG concentration, primarily due to the interaction between PEG's long polymer chains and the hydrogen-bonded network formed with Ferulic Acid. These interactions hinder molecular movement, increasing resistance to flow (Fig. 3)

Ultrasonic velocity increases with PEG concentration, indicating a more rigid and less compressible medium. This is attributed to stronger intermolecular forces—hydrogen bonding and van der Waals interactions—between PEG and Ferulic Acid, which create a tightly bound structure that facilitates faster sound wave propagation (Fig. 5)

As PEG concentration increases, adiabatic compressibility decreases. The dense hydrogen-bonded network restricts the solution's ability to compress, and the space occupied by PEG chains limits molecular flexibility (Fig.7). Higher PEG concentrations result in reduced intermolecular free length due to tighter molecular packing and stronger hydrogen bonding, which decreases the average distance between molecules (Fig.9).

Acoustic impedance ($Z = \rho \times v$) increases with PEG concentration, driven by simultaneous increases in density and ultrasonic velocity. This indicates a denser and more rigid medium with stronger molecular interactions, particularly hydrogen bonding (Fig. 11). These trends agree with previous studies on acoustic properties of polymer-solvent mixtures.

Relaxation time, the duration required for a system to return to equilibrium after disturbance, increases with PEG concentration. Stronger molecular interactions and higher viscosity slow down relaxation processes, with hydrogen bonding contributing to longer recovery times (Fig. 13) [23-24].

Table 1: Experimental values of density, viscosity, and ultrasonic velocity at different temperature

Sample	Density ($Kg.m^{-3}$)				Viscosity ($N.s.m^{-2}$)				Velocity ($m.s^{-1}$)			
	298K	308K	318K	328K	298K	308K	318K	328K	298K	308K	318K	328K
S1	623.123	609.452	606.178	591.89	2.984	2.612	2.238	1.666	1207.20	1156.23	1112.56	1085.00
S2	638.98	627.541	620.79	810.125	3.996	3.425	3.025	2.587	1259.02	1198.11	1145.63	1126.62
S3	649.17	641.451	631.46	825.563	6.230	5.232	5.125	4.289	1299.54	1218.21	1189.55	1175.45

Table 2: Calculated values of adiabatic compressibility free length and acoustic impedance at different temperatures.

Sample	Adiabatic compressibility($N^{-1}.m^{2}$)				Free length(m)				Acoustic impedance($kg.m^{2}.s^{1}$)			
	298K	308K	318K	328K	298K	308K	318K	328K	298K	308K	318K	328K
S1	8.022	8.889	9.231	9.856	0.425	0.489	0.499	0.544	0.824	0.804	0.799	0.758
S2	7.921	8.265	8.745	9.215	0.402	0.454	0.475	0.509	0.901	0.894	0.801	0.797
S3	7.254	7.845	8.213	8.895	0.391	0.439	0.441	0.541	1.021	0.954	0.898	0.825

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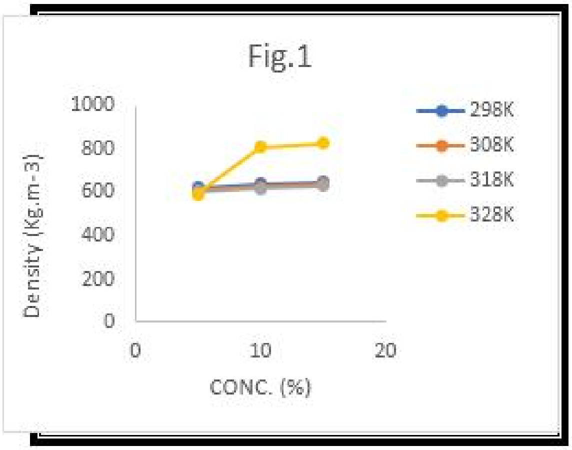

Fig.1 Effect of Temp. on density

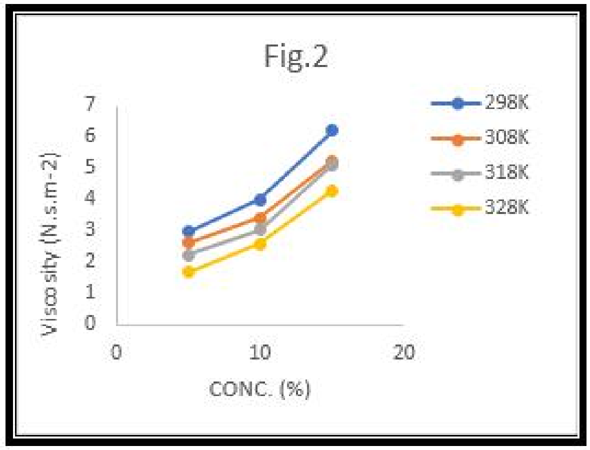

Fig. 2 Effect of Temp. on Viscosity

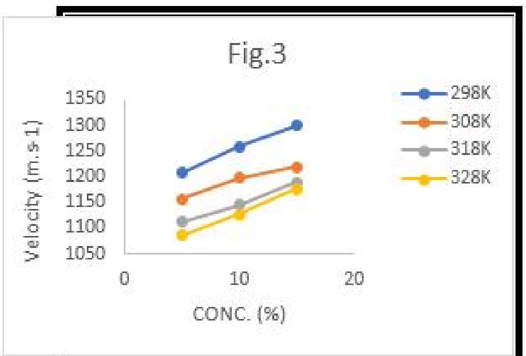

Fig. 3 Effect of Temp. on Velocity

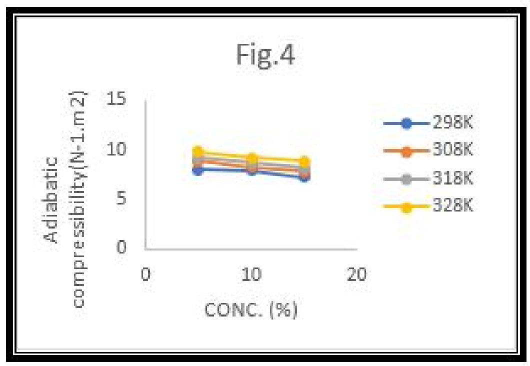

Fig. 4 Effect of Temp. on Adiabatic Compressibility

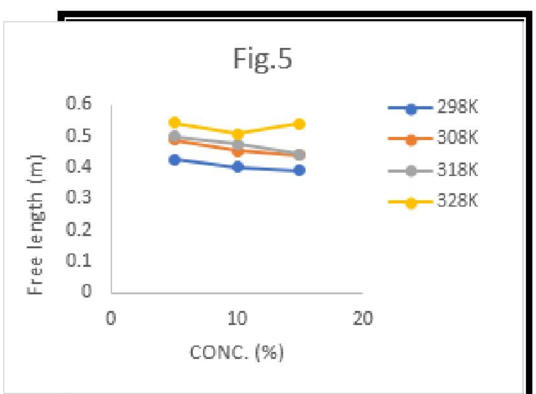

Fig. 5 Effect of Temp. on Free Length

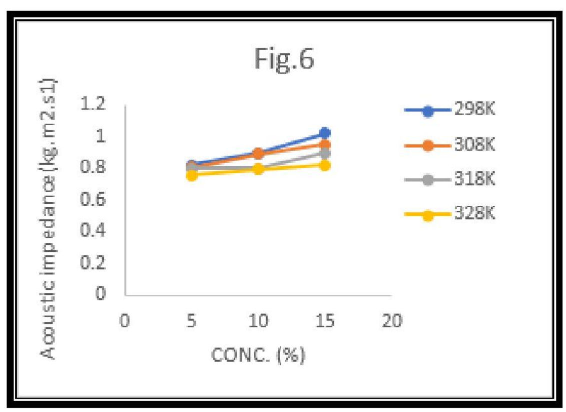

Fig. 6 Effect of Temp. on Acoustic Impedance

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IV. CONCLUSION

This multi-dimensional approach, analysing density, viscosity, ultrasonic velocity, and the calculated thermo-acoustic parameters, offers a comprehensive understanding of the thermophysical and acoustic behaviour of the PEG- Ferulic Acid system.

The novelty of this work lies in its comprehensive evaluation of how these properties simultaneously vary with both temperature and concentration, providing critical data for optimizing coating formulations. The ability to understand and tailor these molecular interactions is particularly relevant for enhancing the performance and durability of coatings in industrial and biomedical applications.

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