Comparative Thermo-Acoustical Study of Cypermethrin and Deltamethrin in acetone at Different Temperatures.

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Abstract:

A comparative ultrasonic investigation of cypermethrin and deltamethrin in acetone has been carried out over a concentration range of 0.02–0.1M and temperature range of (298.15-318.15) K. Density and ultrasonic velocity measurements were used to evaluate acoustical parameters such as adiabatic compressibility, intermolecular free length and acoustic impedance. The variation of these parameters with concentration and temperature were analysed to understand molecular interactions. Density and ultrasonic velocity increase with concentration due to enhanced molecular packing, whereas both decrease with temperature due to thermal expansion and weakening of intermolecular forces. The decrease in compressibility and free length confirms strong solute–solvent interactions. Deltamethrin exhibits stronger interaction behaviour than cypermethrin due to its higher molecular mass and polarizability.

Keywords: Ultrasonic velocity, Density, Temperature effect, Cypermethrin, Deltamethrin, Acoustic parameters, Molecular interactions.

1. Introduction

The study of molecular interactions in liquid mixtures is essential for understanding their physicochemical behaviour and structural organization [1]. Ultrasonic techniques are widely employed due to their sensitivity toward intermolecular forces and structural variations in liquids [2]. Measurements of ultrasonic velocity along with density provide valuable insight into molecular packing, compressibility and interaction strength in liquid systems [3]. Temperature-dependent ultrasonic investigations play an important role in understanding the effect of thermal energy on intermolecular interactions [4]. Variations in acoustical parameters such as adiabatic compressibility and intermolecular free length help in interpreting molecular association and structural rearrangements within liquid systems [5]. Recent investigations on binary mixtures have demonstrated that ultrasonic techniques can effectively describe interaction mechanisms in complex liquid systems. Studies on acoustical parameters in different liquid mixtures have shown that temperature significantly influences intermolecular forces and structural properties [6]. Thermo-acoustical studies have further confirmed that changes in ultrasonic velocity and compressibility can be used to analyse molecular interactions and structural stability of liquid mixtures.

Advanced studies involving nano-dispersed and polymer systems have highlighted the applicability of ultrasonic techniques in diverse chemical systems [7]. Recent developments in thermodynamic and acoustic studies of liquid mixtures have emphasized the importance of combining temperature and concentration effects to understand molecular interactions comprehensively [8]. Ultrasonic investigations on complex systems have shown that these parameters are reliable indicators of solute–solvent interactions [9]. Further studies on thermo-acoustical behaviour in aqueous and non-aqueous systems have demonstrated that acoustic parameters can effectively describe molecular association and interaction strength [10]. Modern research has also explored acoustic and thermodynamic mapping of complex systems which confirming the significance of ultrasonic techniques [11]. Volumetric and ultrasonic studies of liquid mixtures have shown that intermolecular interactions depend strongly on composition and temperature [12]-[13]. Earlier optical and ultrasonic investigations also support the interpretation of molecular interactions in binary mixtures [14]-[15].

Cypermethrin and Deltamethrin are widely used synthetic pyrethroid insecticides employed in agriculture, household pest control, and public health programs. They are highly effective against a broad range of crop pests and mosquito vectors due to their rapid insecticidal action. Their extensive use has increased scientific interest in understanding their physicochemical and molecular interaction behaviour in solvent systems. Such studies are important for evaluating formulation stability, solvation characteristics and transport properties [16]-[17]. Despite extensive work on liquid mixtures, limited studies are available on pesticide–solvent systems. Therefore, the present study focuses on a comparative ultrasonic investigation of pyrethroid pesticides like cypermethrin and deltamethrin in acetone over a wide temperature range.

2. Research Methodology

2.1Materials

Cypermethrin and Deltamethrin (sigma-Aldrich, Merck Group, Germany) of analytical grade (purity ≥ 95%) was used as the solute without further purification. Analytical reagent (AR) grade acetone was used as the solvent throughout the experiment. Density measurements were carried out using a digital densitometer (DMA-35, Anton-Paar, Austria). Ultrasonic multifrequency Interferometer (F-81s, Mittal Enterprises, New Delhi, India) at 2 MHz used for measurement of micrometre reading with temperature controller.

2.2 Sample Preparation

Cypermethrin and deltamethrin solutions were prepared over a molar concentration range of (0.002, 0.004, 0.006, 0.008 and 0.010) mol dm^{-3} in acetone using standard volumetric techniques. Accurately weighed amounts of each pesticide were measured using a precision digital analytical balance (SHIMADZU AUY-220 of accuracy±0.1mg) and subsequently dissolved in acetone in calibrated volumetric flasks to obtain the desired concentrations. The prepared solutions were stored in airtight containers to minimize solvent evaporation and ensure compositional stability. All experimental measurements were carried out at different temperatures (298.15-318.15) K under controlled conditions.

2.3 Experimental

The ultrasonic interferometer cell was thoroughly cleaned and dried prior to each measurement to avoid contamination. Ultrasonic velocity measurements were initially performed for pure acetone using an ultrasonic interferometer (Model F-81_S, Mittal Enterprises, New Delhi, India) operating at a frequency of 2 MHz with an accuracy of ±0.05%, at each experimental temperature to ensure proper calibration of the instrument. Subsequently, measurements were carried out for cypermethrin and deltamethrin solutions over a concentration range of (0.002 to 0.010) mol dm^{-3} and a temperature range of 298.15-318.15K. The measurements were repeated at each temperature, and the entire experimental procedure was performed in triplicate to ensure reproducibility. The average of three independent readings was taken as the final value for each sample at the corresponding temperature. Density measurements of cypermethrin and deltamethrin solutions over a concentration range of (0.002 to 0.010) mol dm^{-3} and a temperature range of (298.15-318.15) K were carryout by using a digital density meter (Anton Paar DMA 35, Austria, accuracy ±0.001gm.cc^{-3}). All measurements were performed at the specified temperatures using a thermostatically controlled water bath.

2.4 Theory

The experimentally measured density (ρ) and ultrasonic velocity (U) values were used to calculate the following acoustical parameters:

$$\text{Adiabatic compressibility } (\beta)\text{: } \beta = \frac{1}{U^2\rho} \tag{1}$$

$$\text{Intermolecular free length } (L_f)\text{: } L_f = K\sqrt{\beta} \tag{2}$$

$$\text{Acoustic impedance } (Z)\text{: } Z = U \times \rho \tag{3}$$

where K is the Jacobson’s constant, which is temperature dependent

3. Results and Discussion

The experimentally measured ultrasonic velocity and density values for cypermethrin–acetone and deltamethrin–acetone systems at different temperatures 298.15-318.15K are presented in Table 1 and Table 2. It shows that, ultrasonic velocity and density increase with increase in concentration at all temperatures. The linear increase of ultrasonic velocity and density with concentration of solute confirmed an increase of cohesive forces because of strong molecular interactions. It suggests powerful dipole-dipole interaction between the component molecules [18]. The addition of pesticide molecules leads to closer packing and reduced intermolecular spacing, facilitating faster propagation of ultrasonic waves. In contrast, ultrasonic velocity decreases with increase in temperature for both systems. This behaviour is attributed to thermal expansion, which increases intermolecular distances and weakens cohesive forces, thereby reducing the velocity of sound propagation [19].

Table1. Ultrasonic velocity (U) and Density (ρ) for cypermethrin-acetone system at different temperature (K).

Concentration (M)	Ultrasonic velocity(ms^{-1})					Density (kg. m^{-3})				
	298.15	303.15	308.15	313.15	318.15	298.15	303.15	308.15	313.15	318.15
0.002	777.639	777.118	776.597	776.075	775.554	1083	1075	1067	1058	1050
0.004	778.349	777.793	777.237	776.681	776.125	1109	1099	1089	1079	1069
0.006	779.058	778.468	777.877	777.287	776.696	1136	1123	1111	1099	1087
0.008	779.768	779.142	778.517	777.892	777.267	1162	1148	1134	1120	1106
0.010	780.477	779.817	779.158	778.498	777.838	1188	1172	1156	1140	1124

Table 2. Ultrasonic velocity (U) and Density (ρ) for Deltamethrin-acetone System at Different Temperature (K).

Concentration (M)	Ultrasonic velocity(ms^{-1})					Density (kg.m^{-3})				
	298.15	303.15	308.15	313.15	318.15	298.15	303.15	308.15	313.15	318.15
0.002	782.528	781.182	779.837	778.491	777.145	1179	1152	1125	1098	1071
0.004	783.148	781.776	780.404	779.032	777.660	1183	1154	1126	1097	1069
0.006	783.768	782.370	780.972	779.573	778.175	1187	1157	1127	1096	1066
0.008	784.388	782.964	781.539	780.115	778.690	1191	1159	1127	1095	1064
0.010	785.008	783.557	782.107	780.656	779.205	1195	1162	1128	1095	1061

The increase in density with concentration reflects greater mass per unit volume and closer molecular packing due to the addition of solute molecules. On the other hand, density decreases with increasing temperature, which is consistent with thermal expansion of the liquid system. Elevated temperatures reduce intermolecular attractions and increase free volume [20]. A comparison between the two systems shows that deltamethrin consistently exhibits higher ultrasonic velocity and density than cypermethrin at all concentrations and temperatures. This behaviour can be correlated with the structural differences between the two pyrethroid pesticides. These structural features enhance cohesive forces and promote tighter molecular packing within the solution.

Thermo-acoustic parameters like adiabatic compressibility (β_{ad}), acoustic impedance (Z) and free length (L_f) for Cypermethrin-acetone and Deltamethrin-acetone system at 303.15K are shown in Table (3).

In both systems, the decrease in adiabatic compressibility and intermolecular free length with increasing concentration indicates stronger solute–solvent interaction and closer molecular packing in the acetone medium. Simultaneously, the increase in acoustic impedance suggests enhanced resistance to ultrasonic wave propagation due to increased structural rigidity and cohesive forces within the solution. However, the magnitude of these parameters differs significantly between cypermethrin and deltamethrin because of their structural differences. Deltamethrin possesses a higher molecular mass, greater structural rigidity, and contains bromine-substituted groups in its molecular framework, whereas cypermethrin contains chlorine substitution and comparatively lower molecular complexity. The presence of bromine atoms increases molecular polarity and intermolecular attraction in deltamethrin, leading to stronger cohesive forces and tighter packing of molecules in the solution. As a result, the deltamethrin system exhibits lower adiabatic compressibility and lower free length than the cypermethrin system, indicating a more compact and less compressible liquid structure.

Table 3. Adiabatic Compressibility (βad), Acoustic Impedance (Z), Free Length (L_f) for Cypermethrin-acetone and Deltamethrin-acetone System at Temperature (303.15K).

Concentration (M)	Cypermethrin			Deltamethrin		
	Adiabatic Compressibility (βad) ($\times10^{10}$ M^2/N)	Acoustic Impedance (Z) ($\times10^5 Kg/m^2.s$)	Free Length (L_f) (A°)	Adiabatic Compressibility (βad) ($\times10^{10}$ M^2/N)	Acoustic Impedance (Z) ($Kg/m^2.s$)	Free Length (L_f) (A°)
0.002	11.14	8.352	0.6990	9.646	8.999	0.6504
0.004	10.64	8.548	0.6833	9.599	9.025	0.6489
0.006	10.18	8.745	0.6682	9.552	9.050	0.6473
0.008	9.744	8.942	0.6537	9.506	9.076	0.6457
0.010	9.336	9.139	0.6399	9.460	9.101	0.6441

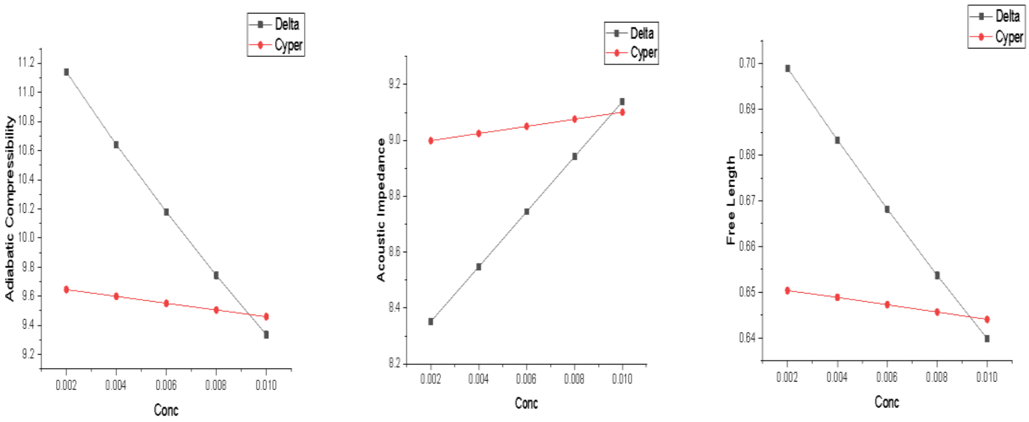

Figure 1. Variation in Acoustical parameters of Cypermethrin (Cyper) and Deltamethrin (Delta) with Concentration at 303.15K.

Furthermore, the stronger intermolecular association in deltamethrin solutions increases the resistance offered by the medium to sound wave propagation, thereby producing higher acoustic impedance values compared to cypermethrin. In contrast, the relatively less rigid and lower molecular weight structure of cypermethrin results in comparatively weaker molecular interaction and slightly higher free space between molecules. Thus, the comparative thermo-acoustical behaviour of both systems strongly depends upon variations in molecular size, polarity, halogen substitution, and structural complexity of the two pyrethroid pesticides.

4. Conclusion

The thermo-acoustical study of cypermethrin–acetone and deltamethrin–acetone systems reveals that increasing concentration enhances intermolecular interactions, as indicated by higher ultrasonic velocity, density and acoustic impedance, along with reduced compressibility and free length. In contrast, increasing temperature weakens these interactions due to thermal expansion. Comparative analysis shows that the deltamethrin system exhibits stronger molecular interactions than cypermethrin, attributed to its higher molecular mass and structural rigidity. Overall, the results demonstrate that ultrasonic techniques are effective for probing molecular interactions in pesticide–solvent systems.

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6. References

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