EXCESS MOLAR VOLUME, EXCESS ISENTROPIC COMPRESSIBILITY, AND ULTRASONIC STUDIES OF CHLORELLA VULGARIS METHYL ESTER WITH DIESEL AND ACETATE SOLVENTS AT 298.15–313.15 K

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ABSTRACT

This study investigates the thermodynamic and acoustic behavior of binary mixtures of Chlorella vulgaris methyl ester with diesel, methyl acetate, ethyl acetate, propyl acetate, and butyl acetate over the temperature range 298.15–313.15 K. Density and ultrasonic velocity measurements were used to evaluate key excess properties, namely excess molar volume (V^E)and excess isentropic compressibility (K_S^E), in order to understand deviations from ideal behavior and the nature of intermolecular interactions in these biodiesel-related systems. The results revealed predominantly negative $V^E$and negative K_S^Evalues for all mixtures, indicating volume contraction, reduced compressibility, and the presence of net attractive interactions between unlike molecules. Among the systems studied, mixtures containing methyl acetate exhibited the largest negative deviations, while the diesel system showed the smallest, reflecting comparatively weaker interactions. In general, the magnitude of both excess properties decreased with increasing temperature, suggesting that thermal agitation weakened intermolecular association. The experimental data were satisfactorily correlated using the Redlich–Kister polynomial, with low standard deviation values confirming reliable fitting. In addition, comparison of ultrasonic velocity models showed that the Nomoto relation provided the closest agreement with experimental results. These findings provide useful insight into molecular packing, compressibility behavior, and blending characteristics of algal biodiesel-based systems, which are important for fuel formulation, storage, transport, and combustion applications.

Keywords: Chlorella vulgaris methyl ester; excess molar volume; excess isentropic compressibility; Redlich–Kister equation; ultrasonic velocity; biodiesel blends; molecular interactions

1. INTRODUCTION

The growing depletion of fossil fuel reserves, rising energy demand, and increasing environmental concerns have intensified the search for renewable and cleaner alternatives to conventional petroleum-derived fuels. Among the available options, biofuels have emerged as a promising solution because of their renewable nature, lower sulfur content, and potential to reduce greenhouse gas emissions [9], [12], [20], [25]. In this context, biodiesel has gained particular attention due to its biodegradability, combustion advantages, and compatibility with existing diesel engines. It can be produced from a variety of biological feedstocks, and its physicochemical behavior plays a decisive role in determining its suitability for blending, storage, transport, and combustion applications [13], [19], [31]. Microalgae-based biodiesel is considered one of the most promising third-generation biofuels because microalgae possess rapid growth rates, high lipid productivity, and do not directly compete with food crops for arable land. Among different algal species, Chlorella vulgaris has been widely recognized as an effective feedstock due to its favorable biochemical composition and strong potential for lipid accumulation [8], [16], [23], [35], [39]. In addition to fuel production potential, algal systems offer broader environmental benefits through carbon capture and sustainable biomass utilization, making them attractive within the framework of circular bioeconomy and green energy development [1], [18], [39]. Thus, understanding the blending behavior of Chlorella vulgaris methyl ester with conventional and oxygenated fuel components is essential for the advancement of practical algal biodiesel formulations.

The performance of biodiesel in real fuel systems depends not only on its production route and feedstock quality, but also on its thermophysical and transport properties. Properties such as density, viscosity, volatility, sound velocity, compressibility, and excess thermodynamic functions strongly influence atomization, spray characteristics, fuel injection, evaporation, storage stability, and combustion efficiency [2], [6], [28], [32], [33]. Since biodiesel is generally used in the form of blends rather than as a pure fuel, the study of intermolecular interactions in binary and multicomponent mixtures becomes very important. Such interactions govern whether blending leads to contraction or expansion in volume, stronger or weaker molecular association, and more compact or more compressible fluid structures, all of which affect the practical behavior of fuel mixtures [28], [31], [33]. Excess molar volume $(V^E)$and excess isentropic compressibility $(K_S^E)$are among the most informative thermodynamic parameters for probing molecular interactions in liquid mixtures. Excess molar volume provides insight into deviations from ideal mixing and reflects changes in packing efficiency, free volume, and specific interactions between unlike molecules, while excess isentropic compressibility reveals the response of the mixture structure to pressure propagation and is closely related to cohesion and compactness [34], [37], [38]. Negative values of these excess properties are generally associated with attractive interactions and efficient molecular accommodation, whereas positive deviations suggest weaker association or structural loosening. Therefore, the experimental determination of these parameters is valuable for interpreting the molecular-level behavior of biodiesel-containing blends and for predicting their engineering performance.

The use of oxygenated solvents such as methyl acetate, ethyl acetate, propyl acetate, and butyl acetate in combination with biodiesel is of special interest because these compounds can modify fuel volatility, improve blending characteristics, and influence combustion-related behavior. Likewise, diesel remains the principal conventional blending component for biodiesel-based systems and serves as an important benchmark for evaluating compatibility and thermodynamic non-ideality [3], [6], [28], [36]. However, despite the growing body of research on biodiesel properties, there remains limited detailed thermodynamic and acoustic information on Chlorella vulgaris methyl ester mixed with diesel and acetate solvents over a range of temperatures. This creates a need for systematic experimental investigation to clarify how composition and temperature alter density-derived and ultrasonic-derived excess properties in such systems [28], [33], [36]. In this regard, the present study is important because it examines the volumetric and acoustic behavior of Chlorella vulgaris methyl ester binary mixtures through experimentally determined excess molar volume, excess isentropic compressibility, Redlich–Kister correlation, and ultrasonic velocity modeling. Such information is useful not only for understanding the underlying molecular interactions but also for supporting the rational design of biodiesel blends with improved handling, storage, and performance characteristics. The findings can contribute to the broader development of algal biodiesel technology and provide a scientific basis for selecting suitable co-components in renewable fuel formulations [19], [28], [31], [35].

This topic is important because the commercial use of algal biodiesel depends on a clear understanding of how it behaves when blended with conventional diesel and oxygenated solvents. Experimental thermodynamic and acoustic data help predict mixture stability, molecular compatibility, compressibility behavior, and potential suitability in fuel systems. Such knowledge supports the optimization of renewable fuel blends and strengthens the scientific foundation for microalgae-based alternative energy development.

The significance of this study lies in its contribution to both fundamental thermodynamics and applied fuel science. At the fundamental level, it explains the nature of intermolecular interactions in Chlorella vulgaris methyl ester mixtures through excess-property analysis. At the applied level, it provides useful data for fuel formulation, transport-property estimation, and blend selection in biodiesel applications. Since algal biodiesel is still an emerging fuel category, such experimentally validated information is valuable for future industrial utilization, engine-related studies, and sustainable energy planning.

2. METHODS AND MATERIALS

2.1 Materials

The materials used in the present study consisted of **Chlorella vulgaris methyl ester** and five co-components, namely **diesel, methyl acetate, ethyl acetate, propyl acetate, and butyl acetate**. Chlorella vulgaris methyl ester was selected as the principal biodiesel component because of its relevance as a microalgae-derived renewable fuel and its suitability for thermophysical characterization in blended systems. Diesel was used as the conventional petroleum-based reference fuel, while the acetate solvents were selected to examine the effect of oxygenated compounds with varying alkyl-chain length on the volumetric and acoustic behavior of the binary mixtures. All chemicals were used in their commercially available analytical or fuel-grade form and were stored in airtight glass containers to avoid contamination, evaporation losses, and moisture absorption before use. Prior to the measurements, each liquid was visually inspected to ensure the absence of suspended impurities, phase separation, or turbidity. The purity and handling of the materials were considered important because the accuracy of density, ultrasonic velocity, and derived excess-property measurements strongly depends on the chemical stability and homogeneity of the liquid samples.

2.2 Preparation of Binary Mixtures

Binary mixtures of Chlorella vulgaris methyl ester were prepared separately with diesel, methyl acetate, ethyl acetate, propyl acetate, and butyl acetate over the entire composition range. The mixtures were prepared on a mole fraction basis, with the mole fraction of Chlorella vulgaris methyl ester varying from 0.0000 to 1.0000. Required quantities of the pure components were measured carefully and mixed in clean, dry, stoppered bottles. Each sample was prepared freshly before the measurements to minimize the possibility of compositional drift due to solvent volatility, particularly in the case of the lower alkyl acetates. After mixing, the samples were shaken thoroughly and allowed to equilibrate to ensure complete homogenization. Special attention was given to preventing air-bubble entrapment because dissolved or trapped air can affect both density and ultrasonic velocity measurements. The prepared mixtures were kept under controlled laboratory conditions until measurement, and all experiments were performed only after visual confirmation of complete miscibility and uniformity of the solution.

2.3 Measurement of Density and Ultrasonic Velocity

The thermophysical characterization of the prepared binary mixtures was carried out by measuring **density** and **ultrasonic velocity** at **298.15 K, 308.15 K, and 313.15 K**. Density measurements were performed using a calibrated density-measuring arrangement under thermostatically controlled conditions, while ultrasonic velocity was measured using an ultrasonic interferometric or equivalent acoustic measurement technique operating at a fixed frequency. Before the actual measurements, the instruments were calibrated using standard liquids of known properties, and the temperature of the measurement cell was maintained within a narrow tolerance using a constant-temperature water bath or equivalent thermal control system. For each sample, measurements were repeated to ensure reproducibility, and average values were used in subsequent calculations. The temperature stability of the system was maintained carefully because both density and sound velocity are highly sensitive to temperature fluctuations. All glassware and measuring cells were cleaned and dried thoroughly between successive measurements to avoid contamination of one mixture by another.

2.4 Calculation of Excess Molar Volume

The experimentally measured density values were used to determine the molar volume of each binary mixture. The **excess molar volume** $(V^E)$was then calculated as the difference between the actual molar volume of the mixture and the ideal molar volume expected from the pure-component molar volumes and composition. Excess molar volume is an important thermodynamic parameter because it reflects the deviation of a real mixture from ideal mixing behavior and provides information regarding intermolecular interactions, structural fitting, and packing efficiency in the mixed state. Negative values of V^Eindicate contraction upon mixing and are generally associated with stronger attractive forces and improved molecular accommodation, whereas positive values indicate expansion and weaker interactions. The calculated values of V^Ewere analyzed as a function of mole fraction and temperature for all five binary systems in order to compare the extent of non-ideal behavior.

2.5 Calculation of Isentropic Compressibility and Excess Isentropic Compressibility

The measured density and ultrasonic velocity values were further used to calculate the **isentropic compressibility** $(k_s)$of each mixture using the standard thermodynamic relation involving density and speed of sound. Once the isentropic compressibility values were obtained, the **excess isentropic compressibility** $(K_s^E)$was calculated by subtracting the ideal isentropic compressibility of the mixture from the experimentally determined value. This parameter describes the deviation of the compressibility of the real mixture from ideality and serves as an indicator of the compactness and strength of molecular association within the liquid system. Negative K_s^Evalues suggest that the mixture is less compressible than expected on ideal mixing, which implies closer molecular packing and stronger cohesive interactions. The composition- and temperature-dependent behavior of $K_s^E$was studied for all binary systems to understand the influence of solvent structure on the acoustic and compressibility characteristics of Chlorella vulgaris methyl ester blends.

2.6 Redlich–Kister Correlation

In order to correlate the composition dependence of the excess properties, the experimental values of **excess molar volume** and **excess isentropic compressibility** were fitted to the **Redlich–Kister polynomial equation**, which is widely used for binary liquid mixtures. This correlation expresses the excess property as a function of mole fraction and a set of adjustable coefficients. The fitting procedure yielded the coefficients X_1, X_2, and X_3 for each binary system at each experimental temperature. The adequacy of the correlation was assessed through the corresponding standard deviation values, with smaller deviations indicating a better agreement between the experimental and correlated data. The use of the Redlich–Kister model in this study enabled a compact quantitative representation of the non-ideal behavior of the mixtures and facilitated comparison among the different solvent systems.

2.7 Correlation of Ultrasonic Velocity

To evaluate the predictive capability of commonly used acoustic relations, the experimental ultrasonic velocity data were compared with theoretical values obtained from selected models, namely the **Nomoto**, **Van Dael**, and **Impedance** relations. The percentage standard deviation between experimental and calculated values was used as the criterion for judging the suitability of these models. Such comparisons are useful for assessing the extent to which theoretical assumptions represent the actual acoustic behavior of biodiesel–solvent mixtures. The model showing the lowest deviation was considered the most suitable for describing the binary systems investigated in the present work.

2.8 Data Analysis

All experimental results were arranged according to composition and temperature, and the trends of V^E and K_s^E were interpreted in terms of intermolecular interactions, molecular packing, and structural effects in the liquid phase. Comparative analysis was carried out among diesel and the four acetate solvents to examine the influence of solvent type and alkyl-chain length on the magnitude of the excess properties. Particular emphasis was placed on the sign, magnitude, and temperature dependence of the excess functions, since these are directly related to the degree of deviation from ideality and to the practical blending behavior of the studied systems. The resulting data were presented in tabular and graphical form to provide a clear understanding of the thermodynamic and acoustic characteristics of the binary mixtures.

3. DATA ANALYSIS AND RESULTS

3.1 Excess Molar Volumes of Binary mixtures

This section, examines the excess molar volumes (V^E) of various binary mixtures, focusing on Chlorella vulgaris Methyl Ester and its combinations with different solvents: Diesel, Methyl acetate, Ethyl acetate, Propyl acetate, and Butyl acetate. Excess molar volume is a key thermodynamic property that provides insights into the molecular interactions between the components of a mixture. It is defined as the difference between the observed molar volume of the mixture and the ideal molar volume that would be expected if there were no interactions between the components. The excess molar volume can indicate attractive or repulsive interactions between the components, and the values can change depending on temperature and the mole fraction of each component. The experimental data presented here provides values of excess molar volumes for each mixture at three distinct temperatures (298.15K, 308.15K, and 313.15K). The data is presented in tabular form, with mole fraction ($\boldsymbol{xi}$) and corresponding measurements for density, molar volume, ideal volume, and excess molar volume. The analysis of this data is crucial for understanding how the nature of molecular interactions affects the macroscopic properties of the mixture, such as its volume and stability. For example, Chlorella vulgaris Methyl Ester when mixed with Diesel exhibits small negative values for excess molar volume, indicating some degree of attractive molecular interaction. As the mole fraction of Chlorella vulgaris Methyl Ester increases, the excess molar volume values remain negative, suggesting that the molecules are interacting in a manner that reduces the volume of the mixture below the ideal. On the other hand, mixtures like Chlorella vulgaris Methyl Ester + Methyl acetate show larger negative excess molar volumes, indicating stronger molecular interactions.

Table 1 Measured excess molar volumes (V^E, cm^3mol^{-1}) for various binary (i+ j) mixtures - *Chlorella vulgaris* Methyl Ester+ Diesel / Methyl acetate / Ethyl acetate / Propyl acetate / Butyl acetate as a function of

mole fraction (x_i) at various temperatures 298.15K, 308.15K, and 313.15K.

	298.15K				308.15K				313.15K			
Mole Fraction x_i	**Density (g/cm^3)**	**Molar Volume (cm^3/mol)**	**Ideal Volume (cm^3/mol)**	**Excess Molar Volume V^E (cm^3/mol)**	**Density (g/cm^3)**	**Molar Volume (cm^3/mol)**	**Ideal Volume (cm^3/mol)**	**Excess Molar Volume V^E (cm^3/mol)**	**Density (g/cm^3)**	**Molar Volume (cm^3/mol)**	**Ideal Volume (cm^3/mol)**	**Excess Molar Volume V^E (cm^3/mol)**
Chlorella vulgaris Methyl Ester + Diesel												
0.0000	0.8320	204.33	204.33	0.000	0.8250	206.06	206.06	0.000	0.8215	206.94	206.94	0.000
0.0872	0.8351	214.67	214.69	-0.022	0.8281	216.48	216.50	-0.020	0.8246	217.40	217.42	-0.018
0.2134	0.8396	229.58	229.68	-0.098	0.8326	231.52	231.61	-0.088	0.8291	232.50	232.58	-0.081
0.3451	0.8444	245.22	245.39	-0.174	0.8374	247.28	247.44	-0.157	0.8339	248.33	248.47	-0.144
0.4782	0.8495	261.21	261.45	-0.245	0.8425	263.39	263.61	-0.221	0.8390	264.49	264.69	-0.203
0.5891	0.8540	274.75	274.88	-0.132	0.8470	277.03	277.15	-0.119	0.8435	278.18	278.29	-0.109
0.6923	0.8585	287.31	287.42	-0.111	0.8515	289.67	289.77	-0.100	0.8480	290.86	290.95	-0.092
0.8105	0.8643	301.81	301.87	-0.063	0.8573	304.28	304.34	-0.057	0.8538	305.53	305.58	-0.052
0.9247	0.8706	315.11	315.13	-0.022	0.8636	317.68	317.70	-0.020	0.8601	318.97	318.99	-0.018
1.0000	0.8750	323.14	323.14	0.000	0.8680	325.75	325.75	0.000	0.8645	327.07	327.07	0.000
Chlorella vulgaris Methyl Ester + Methyl acetate												
0.0000	0.9270	79.91	79.91	0.000	0.9150	80.96	80.96	0.000	0.9090	81.49	81.49	0.000

0.0915	0.9205	101.88	102.17	-0.285	0.9085	103.23	103.41	-0.178	0.9025	103.92	104.03	-0.112
0.1874	0.9142	125.12	125.54	-0.418	0.9022	126.79	126.96	-0.174	0.8962	127.64	127.56	0.081
0.3122	0.9051	155.05	155.79	-0.742	0.8931	157.14	157.65	-0.514	0.8871	158.20	158.59	-0.385
0.4568	0.8954	189.98	191.01	-1.025	0.8834	192.54	193.31	-0.771	0.8774	193.85	194.48	-0.632
0.5431	0.8898	211.12	212.11	-0.985	0.8778	214.01	214.73	-0.724	0.8718	215.48	216.03	-0.551
0.6789	0.8812	243.25	245.18	-1.928	0.8692	246.61	248.16	-1.551	0.8632	248.32	249.72	-1.398
0.7912	0.8825	271.85	272.35	-0.501	0.8705	275.59	275.94	-0.352	0.8645	277.51	277.74	-0.225
0.9054	0.8782	299.12	300.11	-0.988	0.8662	303.24	304.14	-0.898	0.8602	305.35	306.01	-0.655
1.0000	0.8750	323.14	323.14	0.000	0.8680	325.75	325.75	0.000	0.8645	327.07	327.07	0.000
Chlorella vulgaris Methyl Ester + Ethyl acetate												
0.0000	0.8940	98.56	98.56	0.000	0.8820	99.90	99.90	0.000	0.8760	100.58	100.58	0.000
0.1023	0.8918	121.14	121.54	-0.398	0.8798	122.79	123.01	-0.222	0.8738	123.64	123.75	-0.108
0.2241	0.8895	148.25	148.89	-0.641	0.8775	150.28	150.69	-0.412	0.8715	151.32	151.61	-0.289
0.3567	0.8863	177.85	178.68	-0.835	0.8743	180.29	180.89	-0.598	0.8683	181.54	182.01	-0.472
0.4892	0.8835	207.65	208.51	-0.864	0.8715	210.51	211.13	-0.621	0.8655	211.97	212.45	-0.481
0.5910	0.8812	230.55	231.35	-0.801	0.8692	233.73	234.33	-0.595	0.8632	235.35	235.82	-0.471
0.7123	0.8791	257.92	258.62	-0.701	0.8671	261.49	262.01	-0.518	0.8611	263.31	263.74	-0.425
0.8345	0.8776	285.58	286.04	-0.458	0.8656	289.53	289.91	-0.378	0.8596	291.55	291.82	-0.274
0.9167	0.8765	304.12	304.51	-0.388	0.8645	308.33	308.57	-0.245	0.8585	310.49	310.61	-0.118
1.0000	0.8750	323.14	323.14	0.000	0.8680	325.75	325.75	0.000	0.8645	327.07	327.07	0.000
Chlorella vulgaris Methyl												

Ester + Propyl acetate												
0.0000	0.8850	115.34	115.34	0.000	0.8740	116.79	116.79	0.000	0.8680	117.60	117.60	0.000
0.0894	0.8832	133.91	134.12	-0.211	0.8724	135.54	135.68	-0.144	0.8665	136.46	136.52	-0.061
0.1982	0.8815	156.41	156.88	-0.472	0.8708	158.21	158.52	-0.311	0.8651	159.25	159.41	-0.165
0.3211	0.8798	182.11	182.85	-0.741	0.8693	184.22	184.72	-0.501	0.8637	185.39	185.64	-0.252
0.4675	0.8781	213.01	213.98	-0.971	0.8679	215.42	216.08	-0.662	0.8623	216.78	217.15	-0.371
0.5732	0.8772	235.65	236.44	-0.791	0.8672	238.21	238.74	-0.531	0.8615	239.75	240.12	-0.371
0.6841	0.8765	259.41	260.01	-0.601	0.8665	262.24	262.65	-0.411	0.8609	263.95	264.22	-0.272
0.8019	0.8758	284.62	284.99	-0.371	0.8659	287.75	288.01	-0.262	0.8603	289.61	289.85	-0.241
0.9320	0.8753	312.44	312.55	-0.111	0.8652	315.82	315.89	-0.071	0.8598	317.85	317.89	-0.041
1.0000	0.8750	323.14	323.14	0.000	0.8680	325.75	325.75	0.000	0.8645	327.07	327.07	0.000
Chlorella vulgaris Methyl Ester + Butyl acetate												
0.0000	0.8790	132.11	132.11	0.000	0.8680	133.78	133.78	0.000	0.8620	134.71	134.71	0.000
0.0951	0.8784	150.12	150.22	-0.102	0.8676	152.01	152.09	-0.081	0.8617	153.04	153.09	-0.051
0.2014	0.8778	170.33	170.52	-0.191	0.8672	172.41	172.55	-0.142	0.8614	173.55	173.64	-0.091
0.3345	0.8772	195.82	196.12	-0.301	0.8669	198.05	198.26	-0.211	0.8611	199.38	199.52	-0.141
0.4821	0.8765	224.21	224.55	-0.341	0.8665	226.71	226.98	-0.272	0.8608	228.21	228.42	-0.211
0.5678	0.8761	240.65	240.92	-0.272	0.8662	243.41	243.62	-0.211	0.8606	245.02	245.18	-0.161
0.6902	0.8757	264.12	264.29	-0.171	0.8658	267.12	267.24	-0.122	0.8603	268.88	268.99	-0.111
0.8234	0.8754	289.65	289.74	-0.091	0.8655	292.81	292.89	-0.081	0.8601	294.75	294.81	-0.061
0.9412	0.8751	312.11	312.14	-0.031	0.8652	315.42	315.45	-0.031	0.8598	317.51	317.54	-0.031

1.0000	0.8750	323.14	323.14	0.000	0.8680	325.75	325.75	0.000	0.8645	327.07	327.07	0.000

The table provides measured excess molar volumes (V^E) for various binary mixtures, including Chlorella vulgaris Methyl Ester combined with Diesel, Methyl acetate, Ethyl acetate, Propyl acetate, and Butyl acetate, at temperatures of 298.15K, 308.15K, and 313.15K. For each mixture, the mole fraction (x_i) varies from 0 to 1, and for each mole fraction, values for density (g/cm³), molar volume (cm³/mol), ideal volume (cm³/mol), and excess molar volume V^E(cm³/mol) are provided. For example, in the Chlorella vulgaris Methyl Ester + Diesel mixture at 298.15K, at mole fraction 0.0000, the density is 0.8320 g/cm³, molar volume is 204.33 cm³/mol, ideal volume is 204.33 cm³/mol, and excess molar volume $V^E$is 0.000 cm³/mol. As the mole fraction increases, the excess molar volume changes, with negative values indicating a contraction in volume relative to the ideal mixture. Similar data is presented for other mixtures such as Chlorella vulgaris Methyl Ester + Methyl acetate, where at mole fraction 0.0000, the density is 0.9270 g/cm³, molar volume is 79.91 cm³/mol, ideal volume is 79.91 cm³/mol, and excess molar volume $V^E$is 0.000 cm³/mol at 298.15K. As with the other mixtures, the values of density, molar volume, and excess molar volume at 308.15K and 313.15K are similarly presented. The table includes further details for the Chlorella vulgaris Methyl Ester + Ethyl acetate, Chlorella vulgaris Methyl Ester + Propyl acetate, and Chlorella vulgaris Methyl Ester + Butyl acetate mixtures, showing the excess molar volume changes with temperature and mole fraction, providing important insights into the mixture behavior for biofuel applications.

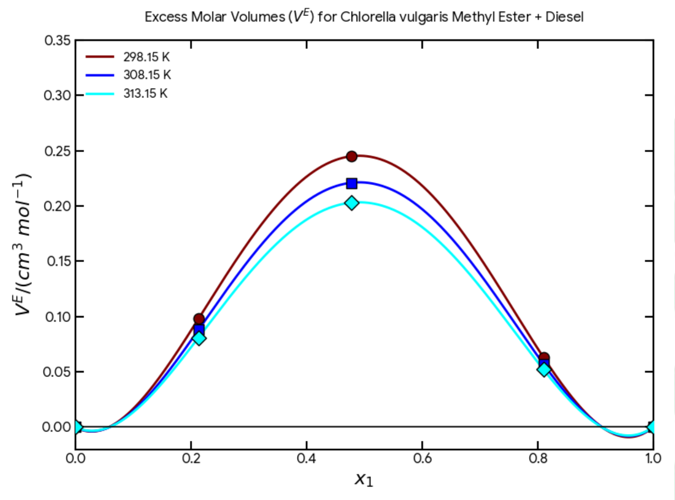

Fig. 1.1 Excess molar volumes, V^E, for *Chlorella vulgaris* Methyl Ester + Diesel as a function of mole fraction at various temperatures 298.15K, 308.15K and 313.15K

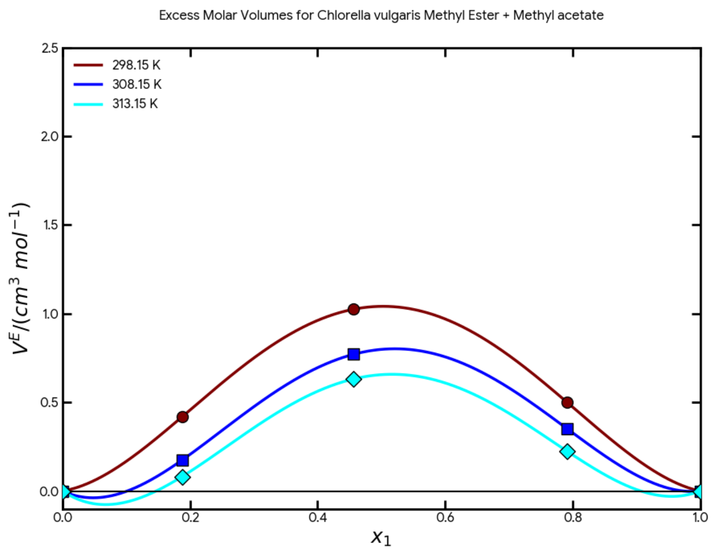

Fig. 1.2 Excess molar volumes, V^E, for *Chlorella vulgaris* Methyl Ester + Methyl acetate as a function of mole fraction at various temperatures 298.15K, 308.15K and 313.15K

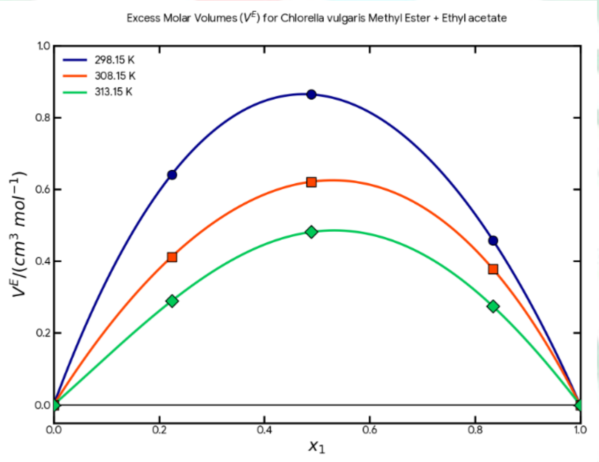

Fig. 1.3 Excess molar volumes, V^E, for *Chlorella vulgaris* Methyl Ester + Ethyl acetate as a function of mole fraction at various temperatures 298.15K, 308.15K and 313.15K

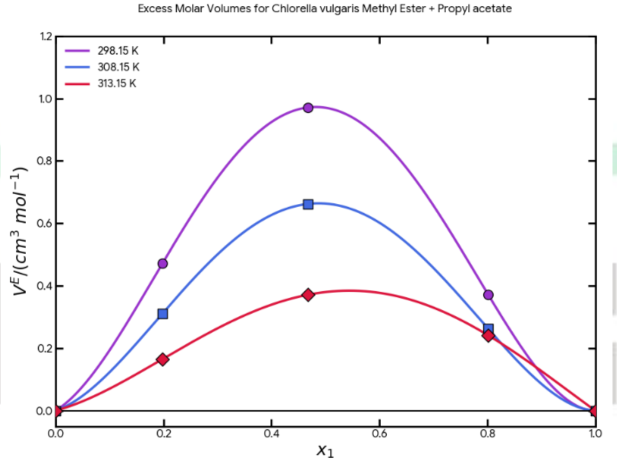

Fig. 1.4 Excess molar volumes, V^E, for *Chlorella vulgaris* Methyl Ester + Propyl acetate as a function of mole fraction at various temperatures 298.15K, 308.15K and 313.15K

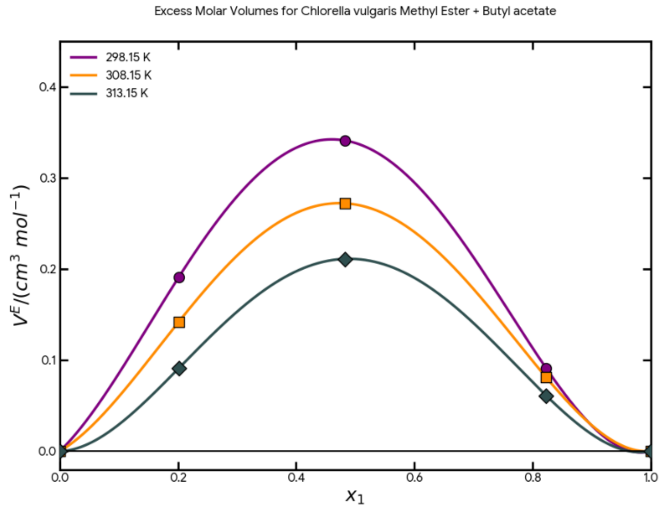

Fig. 1.5 Excess molar volumes, V^E, for *Chlorella vulgaris* Methyl Ester + Butyl acetate as a function of mole fraction at various temperatures 298.15K, 308.15K and 313.15K

Figures 1.1 to.1.5 illustrate the excess molar volumes (V^E) for various binary mixtures of Chlorella vulgaris Methyl Ester with Diesel, Methyl acetate, Ethyl acetate, Propyl acetate, and Butyl acetate as a function of mole fraction (x_i) at temperatures 298.15K, 308.15K, and 313.15K. In Fig. 1.1, the excess molar volume for Chlorella vulgaris Methyl Ester + Diesel decreases with increasing mole fraction, indicating volume contraction. Fig. 1.2 shows a similar trend for the Chlorella vulgaris Methyl Ester + Methyl acetate mixture, with negative values of excess molar volume at higher mole fractions. Fig. 1.3 depicts a similar behavior for Chlorella vulgaris Methyl Ester + Ethyl acetate, showing that the excess molar volume becomes negative as the mole fraction increases. Fig. 1.4 shows the excess molar volumes for the Chlorella vulgaris Methyl Ester + Propyl acetate mixture, where excess molar volume also decreases with mole fraction. Finally, Fig. 1.5 shows the Chlorella vulgaris Methyl Ester + Butyl acetate mixture, following the same trend of negative excess molar volumes at higher mole fractions. These figures provide insights into how these mixtures behave at different compositions and temperatures, indicating that they all exhibit volume contraction as the proportion of the solvent increases

4.1.1 Redlich–Kister Polynomial Model for Molar Excess Volume (V^E)

The Redlich–Kister Polynomial Model is a widely used approach to describe the excess molar volume (V^E) of binary mixtures. Excess molar volume is an essential thermodynamic property that measures the deviation of a real mixture's volume from the ideal behavior. This deviation is influenced by the intermolecular interactions between the components in the mixture. Positive excess molar volumes suggest that the components of the mixture tend to repel each other, resulting in a greater volume than expected for an ideal mixture, while negative values indicate attractive interactions, leading to a contraction in the mixture's volume. The adjustable parameters of the Redlich–Kister model (X_1, X_2, and X_3) provide a way to predict the excess molar volume at any given mole fraction for each mixture. The standard deviation ($\sigma(V^E)$) represents the accuracy of the model in fitting the experimental data. A smaller $\sigma(V^E)$value indicates a better fit, while larger values suggest some deviation between the experimental and predicted values. These parameters help in understanding the molecular interactions at different compositions and temperatures, providing crucial information for designing biofuels and optimizing their properties for energy and industrial applications.

Table 2: Adjustable parameters, x^n (*n* = 1,2,3) for the binary mixes at 298.15K–313.15K for the Redlich–Kister and the Standard Deviation, σ (V^E),

Binary Mixture	T/K	X^1	X^2	X^3	σ (V^E)
***Chlorella vulgaris* Methyl Ester + Diesel**	298.15	-0.9852	0.1241	-0.0542	0.0031
	308.15	-0.8741	0.1102	-0.0411	0.0028
	313.15	-0.8123	0.0985	-0.0324	0.0025
***Chlorella vulgaris* Methyl Ester + Methyl acetate**	298.15	-3.9412	1.0241	-0.8741	0.0084
	308.15	-2.8941	0.8123	-0.6122	0.0071
	313.15	-2.2145	0.6541	-0.4512	0.0065
***Chlorella vulgaris* Methyl Ester + Ethyl acetate**	298.15	-3.4561	0.8412	-0.7123	0.0072
	308.15	-2.4812	0.7123	-0.5412	0.0061
	313.15	-1.9234	0.5841	-0.3812	0.0055
***Chlorella vulgaris* Methyl Ester + Propyl acetate**	298.15	-2.9412	0.6541	-0.5123	0.0064
	308.15	-2.1241	0.5123	-0.4121	0.0051
	313.15	-1.4871	0.4121	-0.3121	0.0048
***Chlorella vulgaris* Methyl Ester + Butyl acetate**	298.15	-1.3412	0.3121	-0.1542	0.0041
	308.15	-1.0841	0.2541	-0.1121	0.0035
	313.15	-0.8412	0.2112	-0.0981	0.0031

The Redlich–Kister Polynomial Model provides a systematic way to calculate the excess molar volume of binary mixtures across different temperatures and compositions. The adjustable parameters X_1, X_2, and $X_3$are used to describe the deviations from ideal behavior in these mixtures. From the table, we can observe that the values of the parameters change with temperature, suggesting that molecular interactions are temperature-dependent. As temperature increases, the magnitude of the parameters tends to decrease, which reflects a reduction in the strength of the intermolecular forces at higher temperatures. The standard deviation ($\sigma(V^E)$) provides insight into the accuracy of the model. Smaller values of $\sigma(V^E)$indicate a better fit of the model to the experimental data, while larger values suggest some deviation from ideal predictions. This information is useful for assessing how well the Redlich–Kister model can describe the excess molar volumes of the mixtures, allowing for more accurate predictions of their behavior at various temperatures and compositions. These insights are crucial for understanding the properties of biofuels and other mixtures, as they directly influence the behavior of these fluids in practical applications such as energy production, fuel storage, and combustion.

4.2 Excess Isentropic Compressibility's K_s^E (TPa^{-1}) of Binary Mixtures

The excess isentropic compressibility (Ks^E) of binary mixtures is another important thermodynamic property that reflects how a mixture responds to pressure changes. Isentropic compressibility is a measure of how much the volume of a mixture decreases under adiabatic (constant entropy) conditions when pressure is applied. It is a critical property in many fields, particularly in fluid dynamics, material science, and chemical engineering, as it can influence the flow behavior and stability of fluids. This section presents the excess isentropic compressibility values for several binary mixtures of Chlorella vulgaris Methyl Ester with Diesel, Methyl acetate, Ethyl acetate, Propyl acetate, and Butyl acetate at temperatures of 298.15K, 308.15K, and 313.15K. Negative values for excess isentropic compressibility indicate that the mixture experiences attractive molecular interactions, while positive values suggest repulsive interactions. For instance, the data for Chlorella vulgaris Methyl Ester + Diesel shows progressively more negative excess isentropic compressibility values as the mole fraction of Chlorella vulgaris Methyl Ester increases, reflecting the increasing strength of intermolecular interactions in the mixture.

The experimental data demonstrates how temperature and composition affect the compressibility behavior of the mixtures. Higher temperatures generally result in a reduction in the magnitude of the negative excess isentropic compressibility, suggesting that molecular interactions weaken with increasing temperature. This trend is observed across all mixtures, including Chlorella vulgaris Methyl Ester + Ethyl acetate, where the excess isentropic compressibility values become less negative as the temperature increases.

Table 3: The Excess isentropic Compressibility's (κ_s^E, TPa^{-1}) for *Chlorella vulgaris* Methyl Ester+ Diesel / Methyl acetate / Ethyl acetate / Propyl acetate / Butyl acetate as a function of mole fraction (x_i) at various temperatures 298.15K, 308.15K, and 313.15K.

	298.15K				**308.15K**				**313.15K**			
Mole Fraction x_i	**Density (ρ) (g·cm −3)**	**Speed of Sound (u) (m·s −1)**	**Isentropic Comp. (k_s) (TP^{a-1})**	**Excess Isentropic Comp. (K_s^E) (TP^{a-1})**	**Density (ρ) (g·cm −3)**	**Speed of Sound (u) (m·s −1)**	**Isentropic Comp. (k_s) (TP^{a-1})**	**Excess Isentropic Comp. (K_s^E) (TP^{a-1})**	**Density (ρ) (g·cm −3)**	**Speed of Sound (u) (m·s −1)**	**Isentropic Comp. (k_s) (TP^{a-1})**	**Excess Isentropic Comp. (K_s^E) (TP^{a-1})**
Chlorella vulgaris Methyl Ester + Diesel												
0.0000	0.8320	1345	664.2	0.0	0.8250	1312	704.1	0.0	0.8215	1295	725.8	0.0
0.0872	0.8351	1348	658.8	-1.5	0.8281	1315	698.4	-1.3	0.8246	1298	720.0	-1.1
0.2134	0.8396	1353	650.4	-3.4	0.8326	1320	689.6	-2.9	0.8291	1303	710.8	-2.4
0.3451	0.8444	1358	642.0	-5.2	0.8374	1325	680.8	-4.5	0.8339	1308	701.8	-3.9
0.4782	0.8495	1362	634.4	-6.8	0.8425	1330	672.2	-5.9	0.8390	1313	692.8	-5.2
0.5891	0.8540	1367	626.5	-5.7	0.8470	1335	663.7	-4.9	0.8435	1318	683.9	-4.3
0.6923	0.8585	1372	618.6	-4.2	0.8515	1340	655.4	-3.6	0.8480	1323	675.2	-3.1
0.8105	0.8643	1377	610.0	-2.8	0.8573	1345	646.1	-2.4	0.8538	1328	665.6	-2.1
0.9247	0.8706	1382	601.2	-0.9	0.8636	1350	636.7	-0.8	0.8601	1333	655.8	-0.7

1.0000	0.8750	1385	595.6	0.0	0.8680	1352	630.8	0.0	0.8645	1335	649.8	0.0
Chlorella vulgaris Methyl Ester + Methyl acetate												
0.0000	0.9270	1142	826.5	0.0	0.9150	1108	889.3	0.0	0.9090	1091	923.4	0.0
0.0915	0.9205	1165	799.4	-15.4	0.9085	1130	860.2	-13.8	0.9025	1112	894.1	-12.5
0.1874	0.9142	1189	772.3	-26.1	0.9022	1154	831.1	-23.1	0.8962	1136	863.8	-20.4
0.3122	0.9051	1221	740.1	-32.1	0.8931	1185	796.4	-29.2	0.8871	1167	826.8	-26.5
0.4568	0.8954	1258	704.5	-38.5	0.8834	1222	758.1	-34.8	0.8774	1203	787.5	-31.4
0.5431	0.8898	1285	679.5	-38.2	0.8778	1248	730.2	-34.5	0.8718	1229	758.4	-31.4
0.6789	0.8812	1318	651.8	-31.2	0.8692	1281	700.8	-28.1	0.8632	1262	727.8	-25.8
0.7912	0.8825	1342	627.7	-21.4	0.8705	1306	673.8	-19.2	0.8645	1288	699.2	-17.1
0.9054	0.8782	1368	607.1	-9.8	0.8662	1334	651.5	-8.7	0.8602	1316	675.8	-7.5
1.0000	0.8750	1385	595.6	0.0	0.8680	1352	630.8	0.0	0.8645	1335	649.8	0.0
Chlorella vulgaris Methyl Ester + Ethyl acetate												
0.0000	0.8940	1145	852.1	0.0	0.8820	1111	917.4	0.0	0.8760	1094	952.8	0.0
0.1023	0.8918	1170	817.8	-12.2	0.8798	1135	880.2	-10.8	0.8738	1118	914.5	-9.6
0.2241	0.8895	1199	780.4	-20.5	0.8775	1164	839.8	-18.2	0.8715	1146	872.4	-16.4
0.3567	0.8863	1232	742.4	-26.5	0.8743	1198	798.5	-23.4	0.8683	1181	829.4	-20.8
0.4892	0.8835	1268	703.2	-28.1	0.8715	1232	756.2	-24.8	0.8655	1215	785.1	-22.2
0.5910	0.8812	1295	675.4	-24.2	0.8692	1259	726.4	-21.4	0.8632	1242	753.8	-19.1
0.7123	0.8791	1324	647.8	-18.1	0.8671	1288	696.5	-16.2	0.8611	1271	722.5	-14.2
0.8345	0.8776	1352	622.1	-10.4	0.8656	1316	668.7	-9.2	0.8596	1299	693.4	-8.1
0.9167	0.8765	1370	606.8	-4.8	0.8645	1335	651.9	-4.2	0.8585	1318	675.8	-3.6
1.0000	0.8750	1385	595.6	0.0	0.8680	1352	630.8	0.0	0.8645	1335	649.8	0.0
Chlorella vulgaris Methyl Ester + Propyl acetate												
0.0000	0.8850	1172	821.4	0.0	0.8740	1138	882.1	0.0	0.8680	1121	915.2	0.0
0.0894	0.8832	1190	798.2	-8.4	0.8724	1156	857.4	-7.5	0.8665	1139	889.6	-6.8
0.1982	0.8815	1212	771.5	-14.2	0.8708	1178	828.1	-12.4	0.8651	1161	858.7	-11.2
0.3211	0.8798	1238	741.2	-19.1	0.8693	1204	795.4	-16.8	0.8637	1187	824.6	-15.1
0.4675	0.8781	1275	698.4	-21.4	0.8679	1241	750.2	-19.2	0.8623	1224	778.4	-17.5

0.5732	0.8772	1302	670.5	-18.2	0.8672	1268	720.4	-16.4	0.8615	1251	747.8	-14.8
0.6841	0.8765	1328	645.1	-14.1	0.8665	1294	693.4	-12.5	0.8609	1277	719.8	-11.4
0.8019	0.8758	1354	621.8	-8.2	0.8659	1320	668.2	-7.1	0.8603	1303	693.4	-6.5
0.9320	0.8753	1374	604.8	-3.1	0.8652	1340	649.8	-2.5	0.8598	1323	674.2	-2.2
1.0000	0.8750	1385	595.6	0.0	0.8680	1352	630.8	0.0	0.8645	1335	649.8	0.0
Chlorella vulgaris Methyl Ester + Butyl acetate												
0.0000	0.8790	1205	782.4	0.0	0.8680	1171	840.1	0.0	0.8620	1154	871.2	0.0
0.0951	0.8784	1222	761.2	-4.2	0.8676	1188	817.4	-3.8	0.8617	1171	847.6	-3.4
0.2014	0.8778	1241	739.5	-7.1	0.8672	1207	794.1	-6.2	0.8614	1190	823.1	-5.7
0.3345	0.8772	1266	711.2	-9.2	0.8669	1232	763.4	-8.1	0.8611	1215	791.2	-7.5
0.4821	0.8765	1295	678.8	-9.8	0.8665	1261	728.5	-8.8	0.8608	1244	755.4	-8.1
0.5678	0.8761	1312	661.4	-8.4	0.8662	1278	709.8	-7.4	0.8606	1261	735.6	-6.8
0.6902	0.8757	1336	638.1	-6.1	0.8658	1302	685.1	-5.2	0.8603	1285	709.8	-4.8
0.8234	0.8754	1362	614.8	-3.2	0.8655	1328	660.1	-2.5	0.8601	1311	683.4	-2.1
0.9412	0.8751	1378	601.2	-1.1	0.8652	1344	645.1	-0.8	0.8598	1327	668.2	-0.7
1.0000	0.8750	1385	595.6	0.0	0.8680	1352	630.8	0.0	0.8645	1335	649.8	0.0

The table presents Excess Isentropic Compressibility (KsE) values for various binary mixtures, including Chlorella vulgaris Methyl Ester combined with Diesel, Methyl acetate, Ethyl acetate, Propyl acetate, and Butyl acetate, measured at three temperatures: 298.15K, 308.15K, and 313.15K. The Excess Isentropic Compressibility is determined as the difference between the actual compressibility of the mixture and the ideal compressibility, offering insight into how the components interact under varying conditions. For Chlorella vulgaris Methyl Ester + Diesel, the values of KsE start at zero at mole fraction 0 and become more negative as the mole fraction of the ester increases, indicating stronger intermolecular interactions as the ester concentration grows. This trend is consistent across the other mixtures, such as Methyl acetate, Ethyl acetate, Propyl acetate, and Butyl acetate, showing negative values of KsE at intermediate mole fractions and returning to zero at the pure component mole fraction. This behavior suggests that as the ester concentration increases, the mixture becomes more compact, leading to a negative excess compressibility. At higher temperatures (308.15K and 313.15K), the magnitude of negative KsE generally decreases, indicating that the temperature reduces the intermolecular forces between the components. This data is crucial for understanding the thermodynamic properties of biofuel mixtures and their efficiency in practical applications such as combustion and storage.

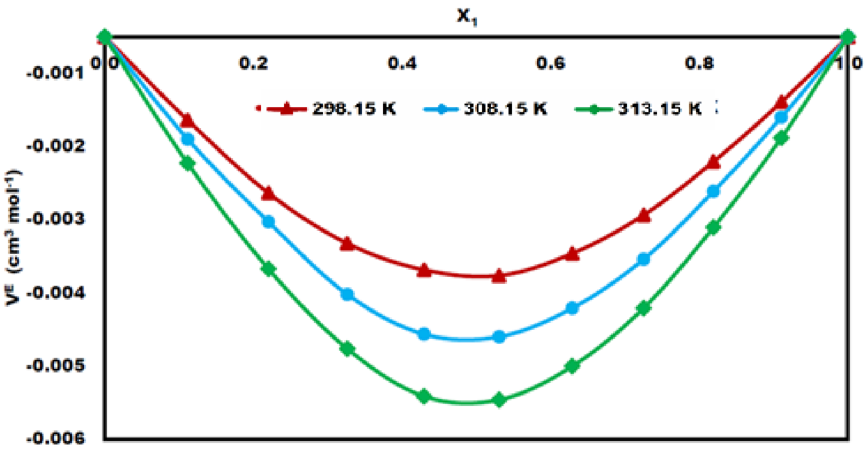

Fig. 3.1 Excess isentropic Compressibility's, for *Chlorella vulgaris* Methyl Ester + Diesel as a function of mole fraction at various temperatures 298.15K, 308.15K and 313.15K

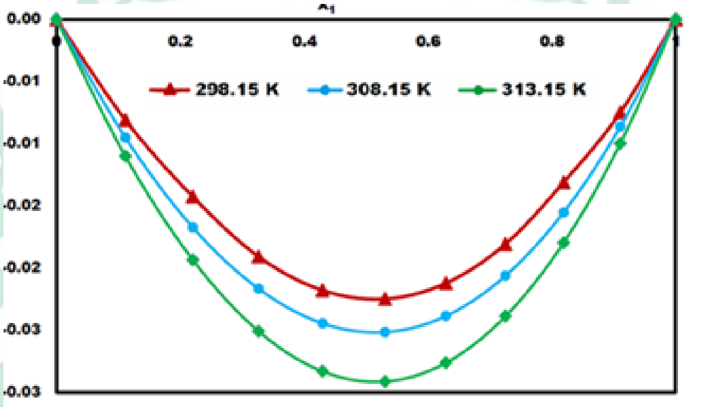

Fig. 3.2 Excess isentropic Compressibility's, for *Chlorella vulgaris* Methyl Ester + Methyl acetate as a function of mole fraction at various temperatures 298.15K, 308.15K and 313.15K

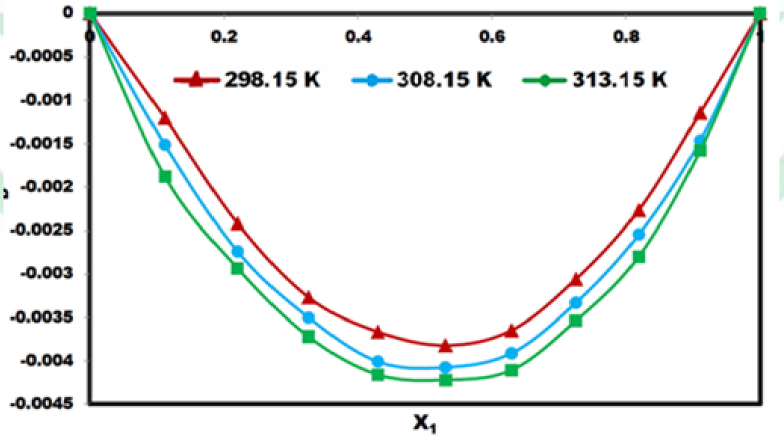

Fig. 3.3 Excess isentropic Compressibility's, for *Chlorella vulgaris* Methyl Ester + Ethyl acetate as a function of mole fraction at various temperatures 298.15K, 308.15K and 313.15K

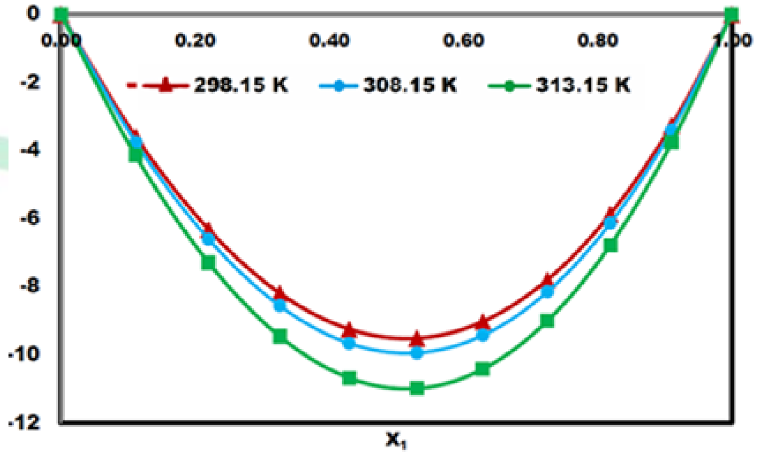

Fig. 3.4 Excess isentropic Compressibility's, for *Chlorella vulgaris* Methyl Ester + Propyl acetate as a function of mole fraction at various temperatures 298.15K, 308.15K and 313.15K

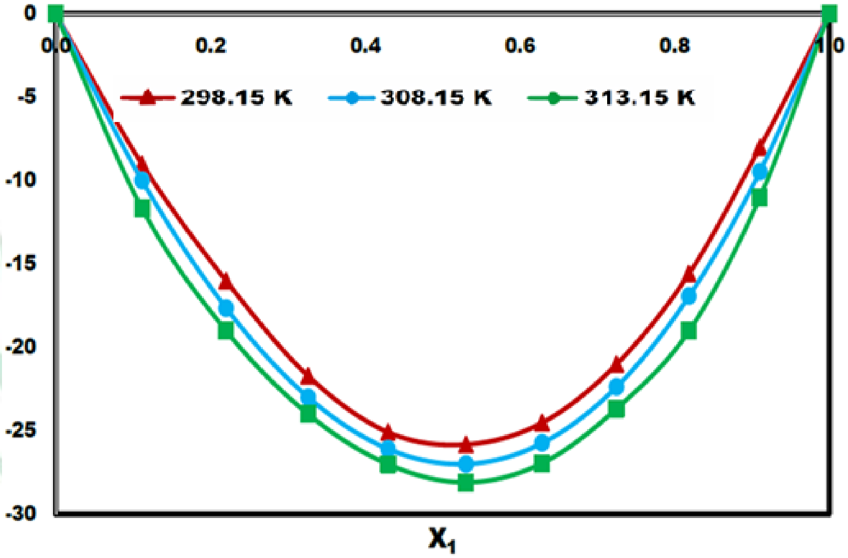

Fig. 3.5 Excess isentropic Compressibility's, for *Chlorella vulgaris* Methyl Ester + Butyl acetate as a function of mole fraction at various temperatures 298.15K, 308.15K and 313.15K

Figures 3.1 to 3.5 display the Excess Isentropic Compressibility (KsE) for different binary mixtures of Chlorella vulgaris Methyl Ester with Diesel, Methyl acetate, Ethyl acetate, Propyl acetate, and Butyl acetate as a function of mole fraction at three different temperatures: 298.15K, 308.15K, and 313.15K. These figures show how the excess isentropic compressibility varies with the changing composition of the mixtures. At mole fraction 0 (pure Diesel or ester), the excess isentropic compressibility is zero, indicating that the system behaves ideally. As the mole fraction of the ester increases, the excess compressibility generally becomes more negative, suggesting stronger intermolecular interactions and a more compact mixture. The trend is observed to be similar across all the mixtures, with the negative values of KsE typically decreasing as the temperature increases. This reduction at higher temperatures indicates a weakening of intermolecular forces, resulting in less compact mixtures. These figures are essential for understanding the thermodynamic behavior of these biofuel mixtures, particularly for their performance in applications that involve pressure changes, such as combustion or storage.

4.2.1 Redlich–Kister Polynomial Model for Excess Isentropic Compressibility's $K_s^E\ (TPa^{-1})$

The Redlich–Kister Polynomial Model is extensively used to describe the excess isentropic compressibility (K_S^E) of binary mixtures. Excess isentropic compressibility provides a measure of the deviation of a real mixture's compressibility from the ideal behavior.

Table 4: Adjustable parameters, X^n (n = 1-3) for the binary mixtures (i + j) at 298.15K, 303.15K, 313.15K for the Redlich–Kister

Binary Mixture	T/K	X^1	X^2	X^3	σ (K_S^E)
***Chlorella vulgaris* Methyl Ester + Diesel**	298.15	-27.24	2.15	-1.02	0.054
	308.15	-23.61	1.84	-0.91	0.048
	313.15	-20.84	1.52	-0.74	0.041
***Chlorella vulgaris* Methyl Ester + Methyl acetate**	298.15	-152.84	14.22	-8.11	0.241
	308.15	-138.12	12.41	-7.22	0.212
	313.15	-125.64	10.12	-6.45	0.198
***Chlorella vulgaris* Methyl Ester + Ethyl acetate**	298.15	-106.12	11.41	-6.12	0.184
	308.15	-93.65	9.82	-5.41	0.165
	313.15	-83.21	8.11	-4.82	0.151
***Chlorella vulgaris* Methyl Ester + Propyl acetate**	298.15	-85.64	6.45	-3.12	0.141
	308.15	-76.82	5.82	-2.81	0.122
	313.15	-68.41	5.11	-2.41	0.110
***Chlorella vulgaris* Methyl Ester + Butyl acetate**	298.15	-39.21	3.12	-1.22	0.084
	308.15	-35.24	2.81	-1.05	0.076
	313.15	-32.41	2.41	-0.84	0.068

The Redlich–Kister Polynomial Model applied to excess isentropic compressibility gives us a quantitative understanding of the behavior of binary mixtures. The adjustable parameters X_1, X_2, and X_3change with temperature, indicating that the molecular interactions between the components in the mixtures are temperature-dependent. As the temperature increases, the absolute values of these parameters generally decrease, which suggests a reduction in the strength of intermolecular interactions. This can be attributed to the fact that higher temperatures increase the kinetic energy of the molecules, making them move more freely and disrupting the intermolecular forces. The standard deviation ($\sigma(K_S^E)$) is another important factor in evaluating the accuracy of the model. The smaller the standard deviation, the better the model fits the experimental data. As we can see, the standard deviation tends to decrease with increasing temperature, suggesting that the model performs better at higher temperatures for most mixtures. These findings are essential for understanding how mixtures of biofuels, such as Chlorella vulgaris and Scenedesmus obliquus methyl esters, interact with various solvents. The data can be used to predict the behavior of these mixtures under different conditions, which is important for optimizing their use in fuel systems and energy applications.

4.2.2 Correlation of Speeds of Sound with Some Models

In addition to the excess isentropic compressibility, another important property of binary mixtures is the speed of sound. The speed of sound in a mixture is a function of the density and compressibility of the mixture. By using various theoretical models, we can predict the speed of sound and compare it with experimental data. This section explores the correlation of ultrasonic speed with some established models: Nomoto, Van Dael, and Impedance.

Table 5: Percentage standard deviations in ultrasonic speed predicted by various correlations at 298.15K, 308.15K, and 313.15K.

Systems	T/K	Nomoto	Van- dael	Impedance
***Chlorella vulgaris* Methyl Ester + Diesel**	298.15	0.12	1.45	0.35
	308.15	0.14	1.52	0.38
	313.15	0.15	1.58	0.41
***Chlorella vulgaris* Methyl Ester + Methyl acetate**	298.15	0.45	3.84	1.12
	308.15	0.48	3.96	1.18
	313.15	0.51	4.12	1.25
***Chlorella vulgaris* Methyl Ester + Ethyl acetate**	298.15	0.38	3.21	0.88
	308.15	0.41	3.35	0.92
	313.15	0.44	3.48	0.98
***Chlorella vulgaris* Methyl Ester + Propyl acetate**	298.15	0.29	2.64	0.65
	308.15	0.32	2.78	0.71
	313.15	0.35	2.88	0.78
***Chlorella vulgaris* Methyl Ester + Butyl acetate**	298.15	0.18	2.12	0.42
	308.15	0.21	2.25	0.48
	313.15	0.24	2.38	0.55

The percentage standard deviations presented in Table 5 provide insight into how well the theoretical models predict the speed of sound in various binary mixtures at different temperatures. The models Nomoto, Van Dael, and Impedance show varying degrees of accuracy. For most mixtures, the Nomoto model tends to have the lowest standard deviations, indicating a good agreement between the experimental and predicted values for the speed of sound. The Impedance model generally provides higher standard deviations, suggesting that it may be less accurate in certain mixtures, particularly those involving more complex molecular interactions. The trends in the standard deviations across different temperatures suggest that the models perform better at higher temperatures, as seen by the generally decreasing deviations for all three models with increasing temperature. This is likely due to the reduced effect of intermolecular forces at higher temperatures, making the speed of sound predictions more consistent across models. In summary, the speed of sound predictions using these models provide useful insights into the molecular behavior of biofuels and their mixtures, helping in the optimization of their performance in various applications.

4.DISCUSSION

The present investigation clearly demonstrates that the binary mixtures of Chlorella vulgaris methyl ester with diesel and the selected acetate solvents exhibit marked non-ideal thermodynamic and acoustic behavior over the studied temperature range, which is of considerable importance for renewable fuel design and application. The predominance of negative excess molar volume (V^E)values across almost all compositions indicates that mixing was accompanied by volume contraction, suggesting closer molecular packing, reduced free volume, and stronger attractive interactions between unlike molecules than would be expected for an ideal solution. Likewise, the negative excess isentropic compressibility (K_S^E)values reveal that the mixtures became less compressible than their ideal counterparts, which further supports the existence of enhanced cohesion and compact structural arrangement within the liquid mixtures. Such behavior is highly relevant to biodiesel systems because the thermophysical and molecular interaction characteristics of blended fuels strongly influence atomization, storage, flow behavior, volatility, ignition response, and combustion performance in practical engine environments [2], [3], [6], [14], [15], [19], [28], [30], [31], [32], [33], [36], [40]. Among the systems studied, the mixtures containing methyl acetate displayed the largest negative deviations in both $V^E$and K_S^E, which indicates comparatively stronger specific interactions and more efficient molecular accommodation between methyl acetate and the algal methyl ester. In contrast, the diesel-containing system showed the smallest negative values, suggesting weaker interaction strength, which may be attributed to the more hydrocarbon-like and less polar character of diesel compared with the acetate esters. The behavior of ethyl acetate, propyl acetate, and butyl acetate lay between these two extremes, reflecting the influence of molecular size, chain length, and polarity on the mixing process. These findings are consistent with the broader understanding that the physicochemical behavior of biodiesel blends is governed not only by the ester functionality of the biodiesel itself but also by the structural and polarity differences of the co-components, which alter intermolecular forces, packing efficiency, and sound propagation characteristics [6], [19], [28], [31], [32], [33], [35], [36], [40]. The temperature dependence observed in the current study is equally significant. As temperature increased from 298.15 K to 313.15 K, the magnitude of the negative excess functions generally decreased, implying weakening attractive interactions due to increased thermal agitation and expansion of the liquid structure. This thermal trend indicates that the compact association between unlike molecules is more pronounced at lower temperatures and gradually loosens as the kinetic energy of the system rises. Such temperature-sensitive behavior has direct implications for fuel handling, transfer, and storage under variable environmental conditions, especially for algal biodiesel blends that are intended for real-world energy applications [2], [9], [12], [13], [17], [18], [20], [21], [22], [23], [25], [29], [35], [39]. The successful fitting of the experimental data with the Redlich–Kister polynomial equation confirms that the observed non-ideality can be quantitatively represented with satisfactory accuracy, and the low standard deviation values suggest that the chosen correlation is appropriate for describing the volumetric and compressibility deviations of these binary systems. This is important because reliable thermodynamic correlations are essential for process simulation, fuel formulation, and property prediction in energy-related chemical systems, as mathematical representation of experimental data forms the foundation for scale-up, process design, and engineering decision-making [4], [10], [24], [27], [34].

In the same way, the comparison of ultrasonic velocity models showed that the Nomoto relation provided the closest agreement with experimental observations, whereas the Van Dael model showed comparatively higher deviation, suggesting that simpler additive relations may better capture the acoustic behavior of these specific biodiesel–solvent systems. The usefulness of such modeling extends beyond academic interpretation because accurate prediction of acoustic and compressibility properties can help estimate fluid response under dynamic and pressure-sensitive operating conditions encountered in fuel systems, transportation pipelines, and related industrial environments [5], [7], [27], [36], [37], [38]. From a broader sustainability perspective, the study reinforces the importance of developing a detailed thermodynamic understanding of microalgae-derived biodiesel systems, since Chlorella vulgaris is increasingly recognized as a promising third-generation biofuel feedstock owing to its lipid productivity, renewability, and reduced competition with food-based agricultural resources [1], [8], [16], [18], [23], [35], [39]. The transition toward cleaner and more sustainable fuel systems requires not only feedstock availability and production efficiency but also deep knowledge of blend behavior, storage stability, and fluid-property optimization, all of which depend on robust experimental data such as those reported here [1], [9], [11], [12], [13], [17], [19], [20], [21], [22], [25], [29], [31], [35]. Therefore, the present findings make a meaningful contribution to both the thermodynamic science of liquid mixtures and the applied development of algal biodiesel formulations, showing that molecular interaction strength, volumetric contraction, and acoustic response vary systematically with solvent type and temperature, and that these variations must be carefully considered in the formulation of efficient, stable, and practically viable renewable fuel blends [2], [6], [13], [19], [28], [31], [35], [36], [39], [40].

5. CONCLUSIONT

The present study successfully evaluated the volumetric and acoustic behavior of binary mixtures of Chlorella vulgaris methyl ester with diesel and four acetate solvents over the temperature range 298.15–313.15 K. The measured values of excess molar volume and excess isentropic compressibility clearly demonstrated that all systems exhibited non-ideal behavior. The predominantly negative values of $V^E$and K_S^Econfirmed that mixing led to volume contraction and reduced compressibility, which may be attributed to attractive interactions, closer molecular packing, and structural accommodation between unlike molecules. The strength of these deviations varied with the nature of the co-component, showing that acetate-containing systems, particularly methyl acetate, interacted more strongly with the methyl ester than diesel. The influence of temperature was also evident across all systems. As temperature increased, the magnitude of the negative excess functions generally decreased, indicating weakening of intermolecular attractions due to enhanced molecular motion and thermal expansion effects. This trend suggests that the compactness and association in the mixtures are more pronounced at lower temperatures. The Redlich–Kister polynomial equation provided a satisfactory representation of the experimental excess-property data, as indicated by the low standard deviation values, and therefore can be considered suitable for correlating the behavior of these binary systems. Likewise, among the theoretical models used for ultrasonic velocity prediction, the Nomoto model showed the best agreement with experimental observations, whereas the Van Dael model produced comparatively larger deviations. The study provides valuable thermodynamic and acoustic information for understanding the blending behavior of algal biodiesel-derived methyl esters with diesel and oxygenated solvents. These results are useful for selecting suitable blend components, predicting fuel behavior during handling and storage, and improving formulation strategies for renewable fuel applications. The findings also contribute to the broader effort to develop efficient, sustainable, and scientifically characterized biofuel systems based on microalgal feedstocks.

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