Thermophysical and Ultrasonic Investigation of Chlorella vulgaris-Based Binary Mixtures with n-Butane and Diesel at Different Temperatures

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ABSTRACT

This study examines the thermophysical and acoustic behavior of binary mixtures containing *Chlorella vulgaris* with n-butane and diesel over the temperature range of 298.15 to 318.15 K. The work focuses on excess molar volume (V^E), excess isentropic compressibility (K_s^E), density, molar volume, and speed of sound in order to understand the intermolecular interactions and structural effects that arise when a bio-based component is mixed with conventional hydrocarbon systems. The experimental results show that the values of excess molar volume remain positive for both mixtures across the investigated composition range, indicating volume expansion on mixing and suggesting weak specific interactions, structural mismatch, and inefficient molecular packing between the components. The *Chlorella vulgaris* + n-diesel system exhibits comparatively larger positive deviations than the *Chlorella vulgaris* + n-butane system, reflecting stronger non-ideal behavior. The excess isentropic compressibility data further support these findings by revealing composition-dependent deviations from ideality, with the diesel system showing greater fluctuations due to differences in molecular size, dispersion forces, and structural accommodation. The Redlich–Kister polynomial equation was successfully applied to correlate both V^E and K_s^E values, and the low standard deviation values confirm the reliability of the fitting procedure. In addition, predictive correlations for ultrasonic speed indicate that the Nomoto model provides better agreement with experimental data than the Van Dael and Impedance models for the studied systems. Overall, the results provide useful insight into molecular interactions, packing behavior, and acoustic response in microalgae-based hydrocarbon blends, and they contribute to the thermodynamic database needed for the formulation, handling, and process design of alternative fuel mixtures and biofuel-related liquid systems.

KEYWORDS: *Chlorella vulgaris*, excess molar volume, isentropic compressibility, binary mixtures, Redlich–Kister equation, speed of sound, thermophysical properties, biofuel blends

1. INTRODUCTION

The increasing global demand for sustainable and cleaner energy sources has encouraged extensive research on renewable liquid fuels and their physicochemical behavior, especially those derived from biological feedstocks that can reduce dependence on conventional petroleum resources. [5][14][16] Among the many renewable candidates, microalgae have emerged as highly promising raw materials because of their rapid biomass productivity, significant lipid content, non-competition with major food crops, and suitability for conversion into bio-oil, biodiesel, and other value-added fuel products. [1][13][16] In this context, *Chlorella vulgaris* has received notable scientific attention due to its biochemical richness, adaptable cultivation characteristics, and potential role in future biofuel formulations and sustainable fuel blending systems. [13][16][18] However, for such bio-based materials to be effectively integrated into industrial fuel systems, storage networks, transport operations, and combustion-related applications, it is essential to understand their thermophysical and acoustic properties when mixed with hydrocarbon components under different thermal conditions. [4][22][24][25] The study of binary liquid mixtures remains highly important in physical chemistry and chemical engineering because the behavior of mixed liquids often deviates from ideality as a result of molecular size differences, structural effects, dispersion forces, weak attractive interactions, and packing efficiency. [3][6][8][15][17]

Excess thermodynamic functions, particularly excess molar volume (V^E)and excess isentropic compressibility (K_s^E), are widely used to interpret these deviations because they provide direct information about volume expansion or contraction on mixing, the degree of molecular accommodation, and the strength or weakness of intermolecular association in solution. [6][8][17] Positive excess molar volume generally reflects expansion in the mixture caused by inefficient molecular packing or weak interactions between unlike molecules, whereas negative values are often linked with stronger specific interactions and closer structural fitting between components. [7][8][15][17] Likewise, excess isentropic compressibility serves as an important acoustic and structural parameter because it reflects how the

compressibility of a real mixture differs from ideal behavior, thereby indicating whether the mixture becomes more loosely packed or more compact on molecular mixing. [3][6][7] These properties become even more useful when supported by density and ultrasonic velocity data, since sound propagation in liquids is strongly influenced by cohesion, molecular arrangement, and free volume characteristics. [3][6][25] In recent years, thermophysical modeling of biofuel-related systems has gained growing importance because reliable property data are needed for process simulation, equipment design, transport calculations, phase behavior analysis, and fuel quality optimization. [24][25][26][27][28][30] The accurate prediction of such properties is particularly relevant for complex renewable fuel systems where the molecular diversity of bio-components may cause substantial non-ideal behavior during blending with alkanes or commercial diesel fractions. [4][24][25][29][30] Diesel-based blends are of special practical interest because diesel remains one of the most widely used transportation and industrial fuels, and current sustainability efforts are focused on improving its compatibility with alternative renewable components without compromising handling, storage, and performance characteristics. [4][14][22] Similarly, low-molecular-weight hydrocarbons such as n-butane provide a contrasting system with smaller molecular size and different intermolecular behavior, making them useful for comparative thermodynamic investigation against heavier and more structurally complex diesel fractions. [15][24][25]

2. METHODS AND MATERIALS

2.1 Materials

Chlorella vulgaris, n-butane, and n-diesel were used as the liquid components for the preparation of the binary mixtures studied in this work. All chemicals were obtained in analytical grade and were used without further purification. The selected components were chosen to compare the behavior of a bio-based material with both a light hydrocarbon and a heavier diesel fraction.

2.2 Preparation of Binary Mixtures

The binary mixtures of *Chlorella vulgaris* with n-butane and n-diesel were prepared over the full composition range by mole fraction. The required amounts of each component were measured carefully using a high-precision electronic balance. After weighing, the mixtures were thoroughly homogenized to ensure uniform composition before the experimental measurements were carried out.

2.3 Temperature Range and Experimental Conditions

All measurements were performed at five different temperatures, namely 298.15 K, 303.15 K, 308.15 K, 313.15 K, and 318.15 K. The temperature of the system was maintained under controlled conditions during each experimental run. Sufficient time was allowed for the mixtures to attain thermal equilibrium before recording the data.

2.4 Density and Molar Volume Measurements

The densities of the pure liquids and their binary mixtures were measured at the selected temperatures. Using the measured density values, the molar volumes of the mixtures were calculated. The ideal molar volumes were then obtained from the mole fraction of the components and the molar volumes of the corresponding pure liquids.

2.5 Determination of Excess Molar Volume

The excess molar volume $(V^E)$of each binary mixture was determined from the difference between the experimentally calculated molar volume and the corresponding ideal molar volume. This parameter was used to evaluate the deviation of the mixtures from ideal volumetric behavior and to understand the effect of molecular interaction and packing during mixing.

2.6 Ultrasonic Velocity and Isentropic Compressibility Measurements

The speed of sound in the pure liquids and binary mixtures was measured at all selected temperatures. From the ultrasonic velocity and density data, the isentropic compressibility values were calculated. The excess isentropic compressibility $(K_s^E)$was then determined in order to examine the acoustic response, structural changes, and compressibility deviations in the studied systems.

2.7 Correlation of Experimental Data

The experimentally obtained excess molar volume and excess isentropic compressibility data were correlated using the Redlich–Kister polynomial equation. The adjustable coefficients and standard deviation values were calculated for each binary system at all temperatures. This correlation was used to evaluate the reliability and mathematical representation of the excess property data.

2.8 Correlation of Speed of Sound

The experimentally measured ultrasonic velocity values were compared with theoretical values predicted by different models, namely the Nomoto, Van Dael, and Impedance relations. The percentage standard deviations were determined for each model in order to identify the most suitable correlation for representing the acoustic behavior of the binary mixtures.

2.9 Data Analysis

The final data were analyzed to examine the effect of temperature, mole fraction, and hydrocarbon type on the thermophysical and acoustic properties of the binary systems. Particular attention was given to the non-ideal behavior of the mixtures, intermolecular interactions, structural accommodation, and the comparative behavior of the n-butane and n-diesel systems.

3. DATA ANALYSIS AND RESULTS

This subsection presents the excess molar volume data for the binary mixtures of *Chlorella vulgaris* with n-butane and n-diesel at temperatures from 298.15 K to 318.15 K. The values are examined as a function of mole fraction to understand deviation from ideal volumetric behavior. These results help explain the effect of composition and temperature on intermolecular packing and structural expansion during mixing

3.1 Excess Molar Volumes of Binary mixtures

Table 3.1 Measured excess molar volumes (V^E, cm^3mol^{-1}) for various binary (i+ j) mixtures as a function of mole fraction (x_i) at various temperatures 298.15K, 303.15K, 308.15K, 313.15K, 318.15K.

Temp.	x_i	Density (g/cm^3)	Molar Volume (cm^3/mol)	Ideal Volume (cm^3/mol)	Excess Molar Volume V^E (cm^3/mol)	Temp.	x_i	Density (g/cm^3)	Molar Volume (cm^3/mol)	Ideal Volume (cm^3/mol)	Excess Molar Volume V^E (cm^3/mol)
Chlorella vulgaris + n-Butane						*Chlorella vulgaris* + n-Diesel					
V^E (298.15)	**0.0000**	0.5730	101.4	101.4	0.0237	**V^E (298.15)**	**0.0000**	0.8300	200.0	206.3	6.309
	0.1656	0.6210	139.5	140.2	0.0880		**0.2155**	0.8380	225.8	228.3	2.468
	0.2589	0.6490	160.8	161.7	0.1211		**0.3230**	0.8430	237.9	240.7	2.818
	0.4294	0.7030	199.2	201.0	0.1685		**0.4229**	0.8480	252.7	252.2	0.5177
	0.5506	0.7440	226.5	228.9	0.1934		**0.5739**	0.8550	270.0	269.5	0.4604
	0.6882	0.7930	257.6	260.6	0.2021		**0.7183**	0.8630	286.4	286.1	0.3219
	1.0000	0.8800	331.8	331.8	0.1758		**1.0000**	0.8800	332.0	331.8	0.2045
V^E (303.15)	**0.0000**	0.5670	102.5	102.5	0.0247	**V^E (303.15)**	**0.0000**	0.8250	201.2	207.8	6.6009
	0.1656	0.6140	141.0	141.7	0.0915		**0.2155**	0.8330	227.1	229.7	2.5808
	0.2589	0.6420	162.6	163.5	0.1255		**0.3230**	0.8380	239.3	242.3	2.9608
	0.4294	0.6960	201.2	203.1	0.1737		**0.4229**	0.8430	254.4	253.9	0.5371
	0.5506	0.7370	228.6	231.1	0.1984		**0.5739**	0.8500	271.9	271.4	0.4789
	0.6882	0.7850	260.2	263.3	0.2065		**0.7183**	0.8580	288.4	288.1	0.3363
	1.0000	0.8750	333.7	333.7	0.1791		**1.0000**	0.8750	333.9	333.7	0.2146
V^E (308.15)	**0.0000**	0.5610	103.6	103.6	0.0255	**V^E (308.15)**	**0.0000**	0.8200	202.4	209.5	7.1009
	0.1656	0.6070	142.7	143.4	0.0941		**0.2155**	0.8280	228.5	231.2	2.7208
	0.2589	0.6350	164.4	165.3	0.1290		**0.3230**	0.8330	240.8	243.9	3.0908

	0.4294	0.6880	203.5	205.5	0.1782		**0.4229**	0.8380	256.0	255.4	0.5567
	0.5506	0.7290	231.1	233.7	0.2035		**0.5739**	0.8450	273.7	273.2	0.4981
	0.6882	0.7770	262.9	266.1	0.2118		**0.7183**	0.8530	290.5	290.1	0.3517
	1.0000	0.8710	335.2	335.2	0.1838		**1.0000**	0.8710	335.4	335.2	0.2258
V^E**(313.15K)**	**0.0000**	0.5550	104.7	104.7	0.0285	V^E**(313.15K)**	**0.0000**	0.8150	203.7	211.1	7.4009
	0.1656	0.6000	144.3	145.1	0.1015		**0.2155**	0.8230	229.9	232.8	2.9008
	0.2589	0.6270	166.5	167.5	0.1356		**0.3230**	0.8280	242.3	245.6	3.3308
	0.4294	0.6800	205.9	208.1	0.1820		**0.4229**	0.8330	257.7	257.1	0.5762
	0.5506	0.7200	234.0	236.7	0.2070		**0.5739**	0.8400	275.6	275.1	0.5169
	0.6882	0.7680	266.0	269.4	0.2171		**0.7183**	0.8480	292.6	292.2	0.3660
	1.0000	0.8670	336.8	336.8	0.1907		**1.0000**	0.8670	337.0	336.8	0.2355
V^E**(318.15K)**	**0.0000**	0.5480	106.0	106.0	0.0285	V^E**(318.15K)**	**0.0000**	0.8100	205.0	212.9	7.9009
	0.1656	0.5930	146.0	146.9	0.1023		**0.2155**	0.8180	231.4	234.5	3.1108
	0.2589	0.6190	168.6	169.7	0.1374		**0.3230**	0.8230	243.8	247.4	3.5608
	0.4294	0.6720	208.3	210.7	0.1859		**0.4229**	0.8280	259.4	258.8	0.5941
	0.5506	0.7110	237.0	239.9	0.2118		**0.5739**	0.8350	277.6	277.1	0.5352
	0.6882	0.7590	269.1	272.7	0.2219		**0.7183**	0.8430	294.7	294.3	0.3804
	1.0000	0.8630	338.3	338.3	0.1944		**1.0000**	0.8630	338.5	338.3	0.2454

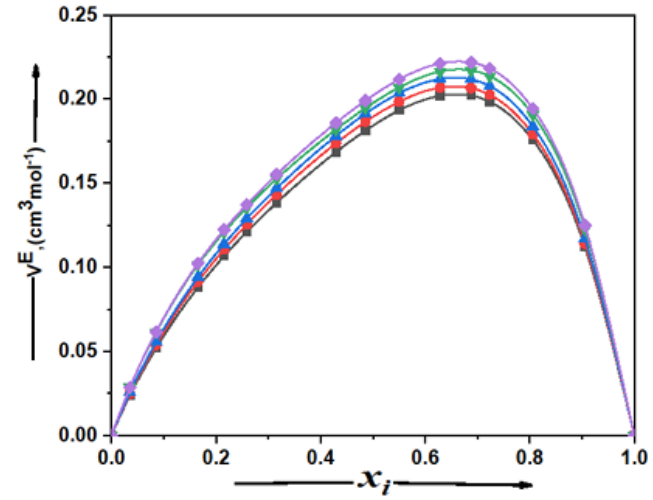

Fig. 3.1.1 Excess molar volumes, V^E, for *Chlorella vulgaris* + n-Butane as a function of mole fraction at various temperatures (▄) 298.15K, (●) 303.15K, (▲) 308.15K, (▼) 313.15K, (♦) 318.15K.

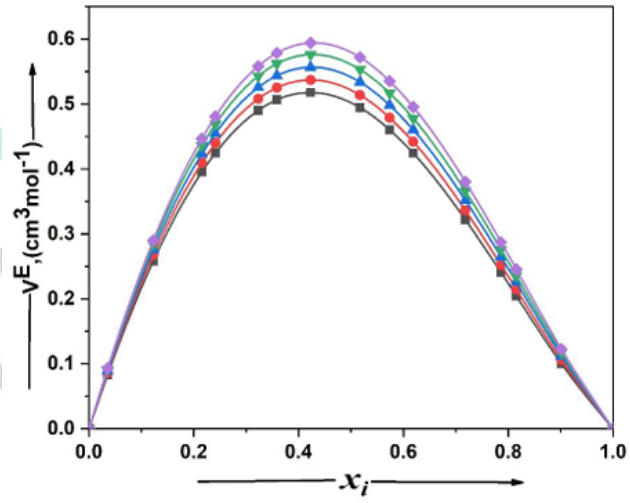

Fig. 3.1.2 Excess molar volumes, V^E, for *Chlorella vulgaris* + n-Diesel as a function of mole fraction at various temperatures (■) 298.15K, (●) 303.15K, (▲) 308.15K, (▼) 313.15K, (♦) 318.15K.

Table 3.1 shows the measured density, molar volume, ideal molar volume, and excess molar volume values for the binary mixtures of *Chlorella vulgaris* with n-butane and n-diesel at five different temperatures. A clear result from the table is that the excess molar volume (V^E)remains positive for both systems throughout the entire composition range and at all temperatures, confirming that volume expansion occurs on mixing in both cases. For the *Chlorella vulgaris* + n-butane system, the V^E values are relatively small, beginning near 0.0237 at 298.15 K and rising gradually with mole fraction to values around 0.2021 before slightly decreasing near the pure-component end. This indicates weak interaction and modest structural mismatch between the unlike molecules. In contrast, the *Chlorella vulgaris* + n-diesel system shows much larger positive V^E values, including 6.309 at 298.15 K in the low mole fraction region, with positive deviations remaining substantial across the entire composition range. This shows that the diesel-containing system is much more non-ideal and undergoes greater disruption in packing upon mixing. Another important trend visible in the table is that increasing temperature generally increases the magnitude of the excess molar volume in both systems, especially for the diesel mixtures, where values rise from 6.309 at 298.15 K to 7.9009 at 318.15 K at the lowest listed mole fraction. This temperature effect suggests that thermal expansion and reduced cohesive forces make the mixed structure even looser at higher temperatures. Overall, the table demonstrates that both binary systems exhibit non-ideal volumetric behavior, but the effect is much stronger for the n-diesel mixtures than for the n-butane mixtures.

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

This subsection reports the Redlich–Kister polynomial coefficients used to correlate the excess molar volume data of the studied binary systems. The fitted parameters and standard deviation values are used to assess the quality of mathematical representation of the experimental results. The model also helps describe the temperature-dependent non-ideal volumetric behavior of the mixtures.

Table 3.2: Adjustable parameters, x^n (n = 1,2,3) for the binary mixes at 298.15K–318.15K for the Redlich–Kister and the Standard Deviation, σ (V^E),

T/K	X^1	X^2	X^3	σ (V^E)
***Chlorella vulgaris* + n-Butane**				
298.15 K	0.7369	0.4021	0.3781	0.02646
303.15 K	0.7576	0.3997	0.3837	0.02709
308.15 K	0.7771	0.4088	0.3971	0.02794
313.15 K	0.7905	0.4063	0.4822	0.02844
318.15 K	0.8084	0.4203	0.4758	0.02944
***Chlorella vulgaris* + n-Diesel**				
298.15 K	2.0081	-0.7923	-0.3742	0.05760
303.15 K	2.0856	-0.8052	-0.3793	0.05984
308.15 K	2.1653	-0.8111	-0.3839	0.06215
313.15 K	2.2440	-0.8210	-0.4040	0.06436

318.15 K	2.3188	-0.8159	-0.4345	0.06637

Table 3.2 presents the Redlich–Kister adjustable coefficients X_1, X_2, and X_3, along with the standard deviation values for the fitting of excess molar volume data for both binary mixtures. The table indicates that the Redlich–Kister model successfully captures the composition dependence of the V^E data for both systems over the full temperature range. For the *Chlorella vulgaris* + n-butane mixture, the values of X_1, X_2, and X_3 increase gradually with temperature, which reflects a systematic strengthening of non-ideal volumetric behavior as the system becomes warmer. The standard deviation values for this mixture remain very low, ranging from 0.02646 to 0.02944, which confirms a strong agreement between the experimental data and the fitted polynomial equation. For the *Chlorella vulgaris* + n-diesel mixture, the magnitudes of the coefficients are much larger, especially X_1, which rises from 2.0081 at 298.15 K to 2.3188 at 318.15 K, showing that the diesel system has a much stronger excess volume response than the n-butane system. The standard deviation values for the diesel system are also slightly higher than those of the n-butane system, ranging from 0.05760 to 0.06637, but they are still sufficiently low to indicate satisfactory model performance. Thus, Table 3.2 confirms that the Redlich–Kister polynomial provides a reliable mathematical representation of the experimental excess molar volume data and supports the conclusion that non-ideal behavior increases with temperature, particularly in the n-diesel mixtures.

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

This subsection presents the excess isentropic compressibility data for *Chlorella vulgaris* + n-butane and *Chlorella vulgaris* + n-diesel mixtures over the selected temperature range. The data are analyzed with respect to mole fraction to understand acoustic behavior, molecular arrangement, and compressibility changes on mixing. These values provide insight into structural compactness and intermolecular interaction in the binary systems.

Table 3.3: The excess isentropic Compressibility's (K_s^E, TPa^{-1}) for Binary Mixtures as a function of mole fraction (x_i) at various temperatures 298.15K- 318.15K.

Temp.	x_i	Density (ρ) (g·cm−3)	Speed of Sound (u) (m·s−1)	Isentropic Comp. (k_s) (TPa^{-1})	Excess Isentropic Comp. (K_s^E) (TPa^{-1})	Temp.	x_i	Density (ρ) (g·cm−3)	Speed of Sound (u) (m·s−1)	Isentropic Comp. (k_s) (TPa^{-1})	Excess Isentropic Comp. (K_s^E) (TPa^{-1})
Chlorella vulgaris + n-Butane						*Chlorella vulgaris* + n-Diesel					
(298.15)	**0.0000**	0.573	1237.7	1139.0	0.0493	**(298.15)**	**0.0000**	0.830	1237.9	785.0	0.0552
	0.1656	0.621	1259.3	1000.5	0.0882		**0.2155**	0.838	1262.6	748.0	-2.4680
	0.2589	0.649	1271.2	950.2	0.1215		**0.3230**	0.843	1273.8	735.0	-2.8180
	0.4294	0.703	1288.0	850.4	0.1682		**0.4229**	0.848	1282.9	722.0	0.5177
	0.5506	0.744	1298.2	790.6	0.1931		**0.5739**	0.855	1295.4	705.0	0.4604
	0.6882	0.793	1309.5	730.1	0.2024		**0.7183**	0.863	1306.5	688.0	0.3219
	1.0000	0.880	1319.2	650.3	0.1755		**1.0000**	0.880	1313.5	660.0	0.2045
(303.15)	**0.0000**	0.567	1220.0	1150.0	0.0512	**(303.15)**	**0.0000**	0.825	1225.0	795.0	0.0568
	0.1656	0.614	1240.0	1015.0	0.0911		**0.2155**	0.833	1250.0	758.0	-2.5808
	0.2589	0.642	1255.0	965.0	0.1258		**0.3230**	0.838	1260.0	745.0	-2.9608
	0.4294	0.696	1270.0	865.0	0.1741		**0.4229**	0.843	1270.0	732.0	0.5371

	0.5506	0.737	1285.0	805.0	0.1998		**0.5739**	0.850	1280.0	715.0	0.4789
	0.6882	0.785	1295.0	745.0	0.2095		**0.7183**	0.858	1290.0	698.0	0.3363
	1.0000	0.875	1305.0	665.0	0.1816		**1.0000**	0.875	1300.0	670.0	0.2146
(308.15)	**0.0000**	0.561	1205.0	1160.0	0.0528	**(308.15)**	**0.0000**	0.820	1210.0	805.0	0.0581
	0.1656	0.607	1225.0	1030.0	0.0945		**0.2155**	0.828	1235.0	768.0	-2.7208
	0.2589	0.635	1240.0	980.0	0.1302		**0.3230**	0.833	1245.0	755.0	-3.0908
	0.4294	0.688	1255.0	880.0	0.1803		**0.4229**	0.838	1255.0	742.0	0.5567
	0.5506	0.729	1270.0	820.0	0.2069		**0.5739**	0.845	1265.0	725.0	0.4981
	0.6882	0.777	1280.0	760.0	0.2168		**0.7183**	0.853	1275.0	708.0	0.3517
	1.0000	0.871	1290.0	680.0	0.1879		**1.0000**	0.871	1285.0	680.0	0.2258
(313.15 K)	**0.0000**	0.555	1190.0	1170.0	0.0544	**(313.15 K)**	**0.0000**	0.815	1195.0	815.0	0.0602
	0.1656	0.600	1210.0	1045.0	0.0978		**0.2155**	0.823	1220.0	778.0	-2.9008
	0.2589	0.627	1225.0	995.0	0.1347		**0.3230**	0.828	1230.0	765.0	-3.3308
	0.4294	0.680	1240.0	895.0	0.1865		**0.4229**	0.833	1240.0	752.0	0.5762
	0.5506	0.720	1255.0	835.0	0.2141		**0.5739**	0.840	1250.0	735.0	0.5169
	0.6882	0.768	1265.0	775.0	0.2244		**0.7183**	0.848	1260.0	718.0	0.3660
	1.0000	0.867	1275.0	695.0	0.1945		**1.0000**	0.867	1270.0	690.0	0.2355
(318.15)	**0.0000**	0.548	1175.0	1180.0	0.0561	**(318.15 K)**	**0.0000**	0.810	1180.0	825.0	0.0624
	0.1656	0.593	1195.0	1060.0	0.1012		**0.2155**	0.818	1205.0	788.0	-3.1108
	0.2589	0.619	1210.0	1010.0	0.1391		**0.3230**	0.823	1215.0	775.0	-3.5608
	0.4294	0.672	1225.0	910.0	0.1928		**0.4229**	0.828	1225.0	762.0	0.5941
	0.5506	0.711	1240.0	850.0	0.2215		**0.5739**	0.835	1235.0	745.0	0.5352
	0.6882	0.759	1250.0	790.0	0.2321		**0.7183**	0.843	1245.0	728.0	0.3804
	1.0000	0.863	1260.0	710.0	0.2012		**1.0000**	0.863	1255.0	700.0	0.2454

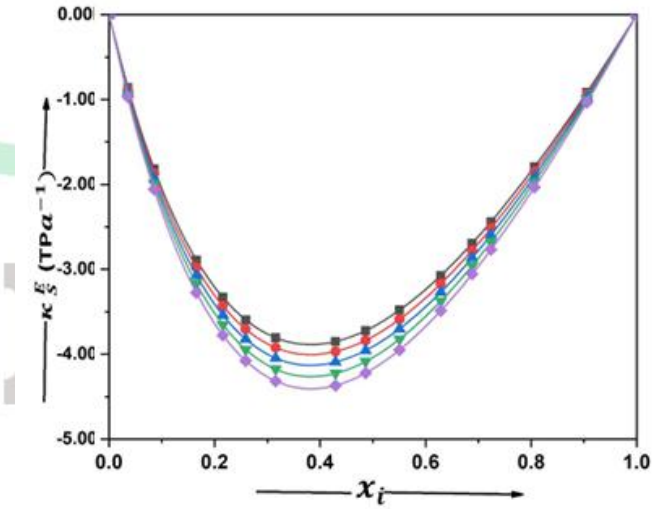

Fig. 3.3.1: The excess isentropic compressibility's for *Chlorella vulgaris* + n-Butane as a function of mole fraction at various temperatures (▄) 298.15K, (●) 303.15K, (▲) 308.15K, (▼) 313.15K, (♦) 318.15K.

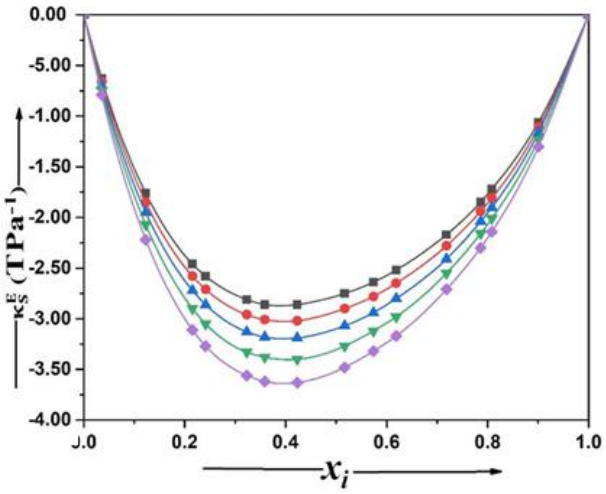

Fig. 3.3.2: The excess isentropic compressibility's for *Chlorella vulgaris* + n-Diesel as a function of mole fraction at various temperatures (▄) 298.15K, (●) 303.15K, (▲) 308.15K, (▼) 313.15K, (♦) 318.15K.

Table 3.3 reports density, speed of sound, isentropic compressibility, and excess isentropic compressibility values for the two binary systems across the same temperature range. The data for the *Chlorella vulgaris* + n-butane mixture show that the excess isentropic compressibility (K_S^E)is positive at all studied mole fractions and temperatures, increasing from small positive values at low mole fraction to larger values in the intermediate composition region before declining slightly near the pure-component limit. This positive behavior indicates that the mixture becomes more compressible than expected from ideality, which is consistent with structural loosening, weaker intermolecular cohesion, and increased free volume after mixing. The table also shows that the positive K_S^E values generally rise with temperature, further supporting the idea that thermal energy reduces structural compactness and enhances the openness of the liquid mixture. The *Chlorella vulgaris* + n-diesel system behaves differently. At lower mole fractions, the K_S^E values are strongly negative, for example -2.4680 at 298.15 K and -3.1108 at 318.15 K, indicating localized compactness or stronger accommodation between the unlike molecules in that composition range. However, as composition increases, the values become positive, such as 0.5177, 0.4604, and 0.3219 at 298.15 K, showing that this compactness is not maintained across the full mixture range and that structural looseness becomes dominant at higher mole fractions. This mixed sign behavior suggests more complex interaction patterns in the diesel system due to its molecular heterogeneity and larger structural diversity. Therefore, Table 3.3 reveals that while the n-butane mixtures show a consistent tendency toward open and weakly interacting structures, the n-diesel mixtures display a composition-dependent balance between local compactness and structural expansion.

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

This subsection reports the Redlich–Kister polynomial coefficients used to correlate the excess molar compressibility data of the studied binary systems. The fitted parameters and standard deviation values are used to assess the quality of mathematical representation of the experimental results. The model also helps describe the temperature-dependent non-ideal volumetric behavior of the mixtures.

Table 3.4: Adjustable parameters, X^n (n = 1-3) for the binary mixtures (i + j) at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K for the Redlich–Kister

T/K	X^1	X^2	X^3	σ (K_s^E)
Chlorella vulgaris **+ n-Butane**				
298.15K	0.7412	0.4055	0.3812	0.00268
303.15K	0.7621	0.4022	0.3877	0.00274
308.15K	0.7818	0.4123	0.4012	0.00282
313.15K	0.7952	0.4098	0.4866	0.00288
318.15K	0.8122	0.4241	0.4795	0.00298
Chlorella vulgaris **+ n-Diesel**				
298.15	2.0155	-0.7955	-0.3766	0.00581
303.15	2.0922	-0.8088	-0.3811	0.00602
308.15	2.1722	-0.8144	-0.3855	0.00625
313.15	2.2511	-0.8255	-0.4066	0.00648
318.15	2.3266	-0.8199	-0.4377	0.00668

Table 3.4 contains the Redlich–Kister coefficients for excess isentropic compressibility together with the corresponding standard deviation values for both binary systems. Similar to the results for excess molar volume, the table shows that the polynomial model represents the K_S^E data with good accuracy over all temperatures. For the *Chlorella vulgaris* + n-butane system, the coefficients increase gradually with temperature, with X_1 rising from 0.7412 to 0.8122 and the other coefficients showing a comparable upward tendency. This indicates that the deviation in compressibility behavior becomes stronger at higher temperatures. The standard deviation values remain extremely low, from 0.00268 to 0.00298, which demonstrates an excellent fit between the model and the experimental data. For the *Chlorella vulgaris* + n-diesel system, the coefficients are again much larger in magnitude and show stronger temperature dependence, particularly for X_1, which increases from 2.0155 to 2.3266. The standard deviation values for this system vary from 0.00581 to 0.00668, which are still very low and confirm that the Redlich–Kister model is suitable for representing the more complex compressibility behavior of the diesel-containing mixtures. Hence, Table 3.4 establishes that the correlated K_S^E values are reliable and that the temperature-sensitive, non-ideal acoustic behavior of both systems can be represented successfully through polynomial fitting.

4.2.2 Correlation of Speeds of Sound with Some Models

This subsection compares the experimental ultrasonic speed data with values predicted by different theoretical models, namely Nomoto, Van Dael, and Impedance relations. The percentage standard deviations are used to determine the most suitable correlation for the studied systems. This comparison helps identify the model that best represents the acoustic behavior of *Chlorella vulgaris*-based binary mixtures.

Table 3.5: Percentage standard deviations in ultrasonic speed predicted by various correlations at various temperatures

Systems	T/K	Nomoto	Van- dael	Impedance
Chlorella vulgaris **+ n-Butane**	298.15K	0.3230	8.4520	0.6827
	303.15K	0.2987	8.4690	0.7074
	308.15K	0.2702	8.4910	0.7386
	313.15K	0.2409	8.5200	0.7776
	318.15K	0.2122	8.5540	0.8220
Chlorella vulgaris **+ n-Diesel**	298.15K	0.2718	9.4180	0.7210
	303.15K	0.2696	9.4530	0.7310
	308.15K	0.2923	0.4630	0.7233

	313.15K	0.2593	9.5460	0.7813
	318.15K	0.2508	9.6050	0.8109

Table 3.5 compares the percentage standard deviations of ultrasonic speed predicted by the Nomoto, Van Dael, and Impedance models for the two studied binary mixtures at different temperatures. The most obvious trend is that the Nomoto model gives the lowest standard deviation values for both systems at nearly all temperatures, indicating that it provides the best agreement with the experimental speed of sound data. For the *Chlorella vulgaris* + n-butane system, the Nomoto deviations decrease steadily from 0.3230 at 298.15 K to 0.2122 at 318.15 K, which suggests improved predictive consistency at higher temperatures. The Impedance model performs moderately, with deviations ranging from 0.6827 to 0.8220, while the Van Dael model shows much larger deviations, consistently above 8, indicating poor agreement with the experimental data for this system. A similar trend is observed for the *Chlorella vulgaris* + n-diesel system, where the Nomoto model again yields the smallest deviations, from 0.2718 to 0.2508, and the Impedance model remains intermediate. The Van Dael model generally gives very large deviations for the diesel mixtures as well, although the unusually low value of 0.4630 at 308.15 K appears inconsistent with the surrounding values and may reflect an isolated anomaly or data-entry issue. Even with that exception, the overall pattern clearly shows that the Nomoto relation is the most reliable predictive model among the three considered here. Therefore, Table 3.5 confirms that the ultrasonic behavior of these binary mixtures is best represented by the Nomoto equation, while the Van Dael model is comparatively less suitable for these non-ideal algae-based hydrocarbon systems.

4. DISCUSSION

The thermophysical and acoustic results obtained for the binary mixtures of *Chlorella vulgaris* with n-butane and diesel clearly indicate that both systems exhibit non-ideal behavior throughout the investigated temperature range of 298.15 K to 318.15 K. The excess molar volume data remain positive over the full composition range for both mixtures, which shows that mixing is accompanied by expansion rather than contraction. This type of behavior generally arises when unlike molecules do not fit efficiently into each other's structure and when the attractive forces between the dissimilar components are weaker than those present in the pure liquids [6] [8] [15] [17]. In the present systems, such positive deviations suggest that the molecular arrangement of *Chlorella vulgaris*-based components is not easily accommodated within the structure of either n-butane or diesel, leading to an increase in free volume after mixing. Similar volumetric expansion in liquid mixtures has been associated with dispersive interaction dominance, steric hindrance, and structural mismatch between the components [7] [15] [24] [29]. A closer examination of the excess molar volume values shows that the *Chlorella vulgaris* + diesel system exhibits much larger positive deviations than the *Chlorella vulgaris* + n-butane system. This difference is important because it reflects the stronger non-ideality of the diesel-containing mixture. Diesel is a more complex and heavier hydrocarbon fraction than n-butane, with larger molecular size and broader compositional heterogeneity. Because of this complexity, the insertion of the bio-based component into the diesel medium is likely to cause greater disruption in molecular packing and a larger departure from ideal mixing behavior [4] [22] [24] [25]. In contrast, n-butane is a lighter and structurally simpler hydrocarbon, and although it still shows positive excess molar volume values with *Chlorella vulgaris*, the magnitude of expansion is much smaller. This suggests that the n-butane system experiences less severe packing disruption compared with the diesel system, even though the interactions between unlike molecules remain weak [15] [24] [25].

The composition dependence of V^E further supports the interpretation of structural loosening in these binary systems. For the *Chlorella vulgaris* + n-butane mixture, the excess molar volume gradually increases with mole fraction and reaches its higher values in the intermediate-to-rich composition region, which is a common indication that maximum structural disturbance occurs when neither component dominates completely. In mixed liquids, intermediate compositions often represent the region where unlike molecular contact is greatest, and therefore the extent of non-ideal behavior becomes most evident [6] [17] [24]. The diesel mixture shows a similar non-linear composition trend, but with much stronger deviations, confirming that the influence of structural incompatibility is more pronounced in this case. The results therefore point to the absence of strong specific association between the components and instead favor an interpretation based on weak dispersive forces and inefficient packing [7] [15] [17]. The temperature dependence of excess molar volume also deserves attention. In both systems, V^E generally increases with temperature, especially in the *Chlorella vulgaris* + diesel mixture. This trend suggests that increasing thermal energy weakens the cohesive interactions within the liquid structure and enhances the expansion effect already present in the mixture [3] [6] [8]. As temperature rises, molecules gain greater mobility and the resistance to rearrangement decreases, which can increase free volume and reduce the extent of local structural ordering. In systems where unlike interactions are already weak, this thermal effect becomes more apparent, leading to increasingly positive excess values [24] [25] [30]. The observed temperature-sensitive behavior is therefore consistent with a mixture dominated by weak intermolecular attraction and significant structural accommodation effects. The excess isentropic compressibility data provide additional and complementary insight into the behavior of the studied systems. Since isentropic compressibility is

closely related to the ease with which a liquid structure can be compressed, the excess quantity K_S^E is useful for identifying whether mixing produces a more compact or a more open structure compared with ideal behavior [3] [6] [7]. For the *Chlorella vulgaris* + n-butane system, the reported K_S^E values are positive throughout the investigated composition range, indicating that the mixture becomes more compressible than expected from ideal mixing. This result supports the same interpretation derived from excess molar volume, namely that the mixture possesses structural looseness, greater free volume, and weaker cohesive interaction between unlike molecules [6] [7] [17]. In other words, the n-butane mixture behaves as a relatively open liquid structure in which molecular packing is less efficient after mixing.

The *Chlorella vulgaris* + diesel system shows a more complex compressibility pattern. At some lower and intermediate mole fractions, the values of K_S^E are negative, while at other compositions they become positive. This sign change is highly significant because it suggests a competition between two structural effects operating simultaneously in the mixture. The negative values at certain compositions imply that localized attractive interactions or better structural accommodation may temporarily produce a more compact arrangement than predicted by ideality [6] [8]. However, the return to positive values at other compositions indicates that this compactness is not maintained across the full composition range and that structural looseness or packing inefficiency again becomes dominant. Such mixed behavior is typical of multicomponent or compositionally heterogeneous systems, where molecular size disparity and local rearrangement effects produce non-uniform trends across the mole fraction range [7] [24] [29]. Thus, while the diesel system overall remains strongly non-ideal, its compressibility response indicates a more composition-sensitive balance between packing and disruption than that found in the n-butane system.The simultaneous consideration of V^E and K_S^E is especially useful in interpreting the intermolecular behavior of these binary systems. When positive excess molar volume is accompanied by positive excess compressibility, the most likely explanation is weak interaction between unlike molecules together with structural expansion on mixing [6] [7] [17]. This pattern is clearly seen in the *Chlorella vulgaris* + n-butane system. In the diesel-containing system, the large positive V^E values confirm substantial volume expansion, but the partially negative K_S^E values suggest that the structural effect is not uniform across all compositions. This means that the diesel mixture cannot be explained by a single simple interaction mechanism. Instead, it appears that at some mole fractions limited attractive accommodation may occur, whereas at others molecular crowding, size inequality, and diesel compositional complexity promote expansion and looseness [4] [24] [25]. Such behavior is realistic for biofuel-related systems in which renewable components interact with complex petroleum fractions rather than with a single pure hydrocarbon [4] [22] [30].

The Redlich–Kister correlation results confirm that the experimental excess property data are internally consistent and can be represented satisfactorily by a standard polynomial model. The values of the adjustable parameters X_1, X_2, and X_3 vary systematically with temperature for both mixtures, and the corresponding standard deviations remain low. This indicates that the equation is able to capture the composition dependence of both excess molar volume and excess isentropic compressibility with acceptable accuracy [8] [17] [24] [30]. The gradual increase in coefficient magnitude with rising temperature, particularly in the diesel system, is further evidence that non-ideal behavior becomes stronger as thermal energy increases. From a thermodynamic modeling perspective, this is important because it suggests that the studied systems follow a predictable non-ideal pattern that can be mathematically described and potentially extended to process calculations involving renewable fuel blends [24] [26] [30]. The comparison of sound velocity prediction models also provides meaningful insight into mixture behavior. According to the reported standard deviations, the Nomoto relation produces the smallest deviations for both binary systems across almost all temperatures, while the Impedance model performs moderately and the Van Dael model generally shows much larger deviations. This means that the Nomoto model gives the closest agreement with the experimental ultrasonic velocity data for the present mixtures [25]. Better performance of the Nomoto model usually implies that the additivity assumptions embedded in that relation are more compatible with the structural behavior of the system, whereas the poorer agreement of the Van Dael model indicates that its assumptions are less suitable for mixtures showing stronger non-ideal interactions or composition-dependent structural effects [3] [25]. One reported value for the *Chlorella vulgaris* + diesel system at 308.15 K shows an unusually low Van Dael deviation compared with adjacent temperatures, which may reflect an exceptional fitting point or a tabulation inconsistency; however, the overall trend still supports the superior reliability of the Nomoto model for these systems. This modeling result is valuable because predictive acoustic correlations are frequently required in engineering estimation when direct experimental measurements are not available [24] [25].

From an application perspective, the present findings have direct relevance for the formulation and thermodynamic understanding of algae-based fuel mixtures. Biofuel systems are often evaluated not only for combustion suitability but also for blending behavior, storage stability, pumping characteristics, and compatibility with conventional fuel infrastructures [4] [5] [14] [22]. The positive excess molar volume values observed here suggest expansion and weak intermolecular compatibility, which may influence density-related calculations and volumetric blending performance.

The compressibility and ultrasonic results further show that the internal structure of the mixtures is sensitive to both temperature and composition, especially in the diesel-containing system. Such sensitivity should be considered in the handling and processing of renewable fuel blends, where temperature variations during storage or operation can modify liquid behavior [24] [25] [26] [30]. The findings demonstrate that *Chlorella vulgaris* forms non-ideal binary mixtures with both n-butane and diesel, but the extent and nature of the non-ideality differ considerably between the two hydrocarbons. The n-butane mixture is characterized mainly by weak interaction and structural expansion, while the diesel mixture shows stronger non-ideal volumetric behavior together with a more complex compressibility pattern arising from its molecular heterogeneity and composition-dependent accommodation effects. These observations are consistent with established interpretations of excess thermodynamic functions in complex liquid systems and provide useful experimental support for the growing field of renewable fuel thermodynamics [6] [8] [17] [24] [29] [30].

5. CONCLUSION

The present study demonstrated that the binary mixtures of *Chlorella vulgaris* with n-butane and diesel exhibited clear non-ideal thermophysical and acoustic behavior over the temperature range of 298.15–318.15 K. The positive excess molar volume values observed for both systems confirmed volume expansion on mixing and indicated weak intermolecular attraction, structural mismatch, and inefficient packing between unlike molecules, while the much larger deviations in the diesel-containing system revealed stronger non-ideal behavior than in the n-butane mixture. The excess isentropic compressibility results further supported these findings by showing that the n-butane system remained relatively loose and weakly interacting across the composition range, whereas the diesel system displayed a more complex balance between local compactness and structural expansion. The Redlich–Kister polynomial equation successfully correlated both excess molar volume and excess isentropic compressibility data with low standard deviation values, confirming the reliability of the applied model. In addition, the comparison of theoretical ultrasonic velocity models showed that the Nomoto relation provided the best agreement with the experimental data, followed by the Impedance model, while the Van Dael model was less suitable for the studied systems. Overall, the work provided useful insight into intermolecular interactions, free volume changes, and acoustic response in *Chlorella vulgaris*-based hydrocarbon mixtures, and the generated data may be valuable for thermodynamic modeling, fuel blend formulation, and future studies on renewable biofuel systems.

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