

Thermoacoustic Properties of Ethanol–n-Hexane and 1-Propanol–n-Hexane Binary Mixtures: A Comparative Study at 298.15 K

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Abstract

Using an Anton Paar DSA 5000 M instrument, measurements of density, sound velocity, and viscosity were carried out for ethanol–n-hexane and 1-propanol–n-hexane binary mixtures across mole fractions ranging from 0.1 to 0.9 at a constant temperature of 298.15 K. These binary mixtures were specifically selected to investigate the behavior of polar–nonpolar molecular interactions and how they affect the thermophysical properties of the system. The density, sound velocity, and viscosity data were accurately measured under controlled experimental conditions, ensuring high precision and reproducibility. From the measured experimental data, several important thermodynamic and acoustic parameters were calculated, including isentropic compressibility (κ_s), acoustic impedance (Z), free length (L_f), free volume (V_f), and internal pressure (π). The analysis of these derived parameters provides valuable insights into molecular interactions within the mixtures. In particular, the isentropic compressibility and acoustic impedance are sensitive to molecular packing and interaction strength, while free volume and internal pressure reflect the molecular mobility and cohesion forces present. The variation of these parameters with changing mole fraction highlights the non-ideal behavior arising due to non-covalent interactions, such as hydrogen bonding, van der Waals forces, and dipole-induced interactions, between alcohol and n-hexane molecules. Comparative analysis between ethanol–n-hexane and 1-propanol–n-hexane systems shows how chain length and molecular structure influence the extent of interaction. The results revealed that alcohols with longer alkyl chains (1-propanol) exhibited stronger deviation from ideal mixing compared to ethanol, indicating enhanced molecular interactions. These findings contribute to a better understanding of solution thermodynamics and can be applied in fields, such as chemical engineering, formulation science, and process optimization, where precise knowledge of mixture behavior is critical.

Keywords: Intermolecular non-covalent interactions, acoustic impedance, internal pressure

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INTRODUCTION

A clear understanding of the structural characteristics and molecular interactions in liquid mixtures is important from both theoretical and applied perspectives. The study of fundamental thermodynamic and thermo-acoustic properties offers valuable insights into the deviations from ideal behavior observed in complex systems. These properties reflect the influence of intermolecular forces such as dipole–dipole interactions, van der Waals attractions, and hydrogen bonding between unlike molecules. Beyond their scientific significance, they also hold practical value, contributing to the development of predictive thermodynamic models that are essential for

improving processes in diverse industries, including chemicals, food, pharmaceuticals, petrochemicals, and coatings [1, 2]. Ultrasonic velocity studies of mixtures comprising polar and nonpolar components, which are widely utilized in industrial and technological fields, offer a sensitive approach to investigate molecular interactions [3–5]. Acoustic and thermodynamic studies of liquid mixtures provide valuable insights into molecular packing, dynamic behavior, and the strength of intermolecular interactions. Ethanol serves as a key industrial solvent and an essential feedstock for the synthesis of various organic compounds such as diethyl ether, ethyl halides, acetic acid, esters, etc. [6, 7]. Owing to its molecular structure, ethanol is frequently regarded as a “universal solvent,” since it can effectively dissolve a wide range of substances, both polar (hydrophilic) and nonpolar (hydrophobic) in nature [8]. In the pharmaceutical industry, propanol serves chiefly as a solvent for resins and cellulose esters, with limited application as a disinfectant [9–11]. On the other hand, n-hexane, a nonpolar hydrocarbon, is widely used as a recrystallization medium because many organic compounds exhibit high solubility in hot n-hexane but limited solubility at lower temperatures [12, 13].

In the present work, molecular interactions in mixtures of polar and nonpolar solvents are investigated with particular emphasis on the effect of varying the parent carbon chain. Since the occurrence of hydrogen bonding in mixtures where n-hexane acts as the common component is minimal, the study primarily examines other non-covalent forces that govern the behavior of these systems. Measurements of density (ρ), ultrasonic velocity (U), and viscosity (η) were carried out for the binary mixtures of ethanol–n-hexane and 1-propanol–n-hexane at 298.15 K, across mole fractions ranging from 0.1 to 0.9, to examine the factors responsible for deviations from ideal behavior. Based on the experimental data of velocity, viscosity, and density, several derived thermodynamic and acoustic parameters, including acoustic impedance, isentropic compressibility, free volume, internal pressure, and free length, were evaluated and analyzed to gain insight into the nature of molecular interactions within these mixtures [14, 15].

MATERIAL AND METHODS

The objective of this study was to measure ultrasonic velocity (U), viscosity (η), and density (ρ) of binary liquid mixtures at 298.15 K across mole fractions ranging from 0.1 to 0.9. From the experimental data, key thermodynamic and acoustic parameters, namely isentropic compressibility (β_a), acoustic impedance, free length, free volume (V_f), and internal pressure (π_i), were evaluated. These parameters were further analyzed to provide insights into the strength and nature of intermolecular interactions in the studied mixtures.

The solvents employed were ethanol (CAS 64-17-5), 1-propanol (CAS 71-23-8), and n-hexane (CAS 110-54-3), all obtained from Merck KGaA, Darmstadt, Germany, with a minimum purity of 99.8% and used without further purification.

Density, viscosity, and ultrasonic velocity measurements were carried out using an Anton Paar DSA 5000 M instrument. The instrument provides high-precision measurements, with density accurate to $\pm 0.000007 \text{ g cm}^{-3}$ (up to 3 g cm^{-3}) and ultrasonic velocity in 1000–2000 m s^{-1} range with an accuracy of $\pm 0.01 \text{ m s}^{-1}$, and viscosity over 0.2 to 30,000 $\text{mm}^2 \text{ s}^{-1}$ with an accuracy of $\pm 0.1\%$. The operating temperature spans from 0 to 100°C, with a repeatability of $\pm 0.001^\circ\text{C}$. Measurements are based on the oscillation period of a quartz U-tube containing air, solvent, or the solution under study [16].

Before each run, the U-tube was rinsed with acetone and subsequently dried by passing moisture-free air through it using an air pump. Drying was continued until a constant oscillation period was observed, confirming stability, as performed during the initial calibration of the instrument.

RESULTS AND DISCUSSION

The experimental values of density, ultrasonic velocity, and viscosity for pure ethanol, 1-propanol, and n-hexane at 298.15 K, together with literature data and standard deviations, are presented in Table

1. The measured properties of the binary mixtures density (ρ), viscosity (η), and ultrasonic velocity (U), along with the derived thermodynamic and acoustic parameters, namely isentropic compressibility, acoustic impedance, free length, free volume, and internal pressure, are summarized in Tables 2 and 3 for ethanol–n-hexane and 1-propanol–n-hexane systems, respectively. The variations in these parameters are analyzed to gain insight into the molecular interactions present in the mixtures.

Table 1. Density (ρ), ultrasonic velocity (u), and viscosity (η) of ethanol, 1-propanol and n-hexane at 298.15K.

298.15 K	Lit	ρ (g cm ⁻³)	δ	Lit	u (m s ⁻¹)	δ	Lit	η (mPa.s)	δ
Ethanol	0.78950 [17]	0.790173	6.73 x 10 ⁻⁴	1161.78 [18]	1161.82	0.04	1.1870 [19]	1.18635	6.5 x 10 ⁻⁴
1-Propanol	0.79960 [20]	0.799601	1.00 x 10 ⁻⁶	1205.93 [21]	1205.85	0.08	2.1178 [20]	2.11800	2.0 x 10 ⁻⁴
n-Hexane	0.65521 [12]	0.655214	4.00 x 10 ⁻⁶	1076.30 [22]	1075.72	0.58	0.3036 [23]	0.30369	9.0 x 10 ⁻⁵

Table 2. Ethanol–n-hexane system.

C (M.F.)	P (kg m ⁻³)	U (m s ⁻¹)	η (mPa.s)	$\beta_a \times 10^{-10}$ (cm ² /dyne)	Z (g/cm ² sec)	$L_f \times 10^{-11}$ (cm ² /dyne)	$V_f \times 10^{-8}$ (cm ³ /mol)	$\pi_i \times 10^8$ (dyne/cm ²)
0.1	761.58	1125.1	0.9208	10.360	857384.3	6.3307	4.1771	8.7659
0.2	741.45	1099.8	0.7342	11.159	815133.9	6.5702	5.8618	7.3060
0.3	716.48	1081.2	0.7097	11.927	775064.7	6.7925	8.9449	5.9138
0.4	704.97	1072.7	0.6043	12.339	755876.4	6.9089	10.267	5.3446
0.5	694.74	1064.5	0.6007	12.701	739582.2	7.0095	14.200	4.5561
0.6	683.02	1060.3	0.4798	13.020	724276.1	7.0972	15.557	4.2016
0.7	664.25	1057.9	0.4177	13.469	702271.2	7.2184	23.585	3.4596
0.8	667.52	1059.1	0.3824	13.353	707028.5	7.1873	31.513	3.0425
0.9	660.059	1064.30	0.3416	13.375	702500.9	7.1931	39.050	2.7192

Table 3. 1-propanol–n-hexane system.

C (M.F.)	P (kg m ⁻³)	U (m s ⁻¹)	η (mPa.s)	$\beta_a \times 10^{-10}$ (cm ² /dyne)	Z (g/cm ² sec)	$L_f \times 10^{-11}$ (cm ² /dyne)	$V_f \times 10^{-8}$ (cm ³ /mol)	$\pi_i \times 10^8$ (dyne/cm ²)
0.1	775.80	1180.8	1.6073	9.2508	915797.8	5.9822	3.5291	8.0814
0.2	755.73	1154.9	1.2144	9.9259	872573.3	6.1966	5.5262	6.6553
0.3	736.82	1131.1	0.9323	10.608	833438.0	6.4059	8.4483	5.5341
0.4	719.67	1114.3	0.7263	11.179	802322.6	6.5762	12.723	4.6346
0.5	704.85	1102.2	0.5719	11.671	777160.8	6.7193	18.907	3.9099
0.6	691.21	1093.1	0.4660	12.096	755980.9	6.8404	26.764	3.3579
0.7	679.03	1086.9	0.4000	12.482	737569.7	6.9489	35.048	2.9652
0.8	668.99	1081.8	0.3559	12.782	723411.7	7.0318	43.579	2.6711
0.9	660.770	1077.9	0.3241	13.031	712105.2	7.0999	52.312	2.4407

Figure 1 shows that the density of the ethanol–n-hexane system is lower than that of the 1-propanol–n-hexane system. In general, an increase in the carbon chain length enhances the solubility of organic molecules in nonpolar solvents. Since 1-propanol has a longer chain than ethanol, it favors better solubility of n-hexane, which contributes to the higher density observed. The additional –CH₂ group in 1-propanol also promotes stronger molecular orientation and packing within the mixture, leading to an overall increase in density compared with the ethanol–n-hexane system. Another factor contributing to the higher density of the 1-propanol–n-hexane system is the intrinsic density of 1-propanol itself, which is greater than that of ethanol, and consequently increases the overall density of its mixtures [24, 25].

Figure 2 indicates that the viscosity of the 1-propanol–n-hexane system is higher than that of the ethanol–n-hexane system. Viscosity is strongly influenced by molecular structure; the additional $-\text{CH}_2$ group in 1-propanol increases intermolecular friction, resulting in greater resistance to flow and, consequently, higher viscosity in the mixture [26–28].

Similarly, Figure 3 shows that ultrasonic velocity is higher in the 1-propanol–n-hexane system. Since sound velocity in liquids is directly related to density, the greater velocity observed can be attributed to the higher density of the 1-propanol–n-hexane mixtures compared with those containing ethanol [29–31].

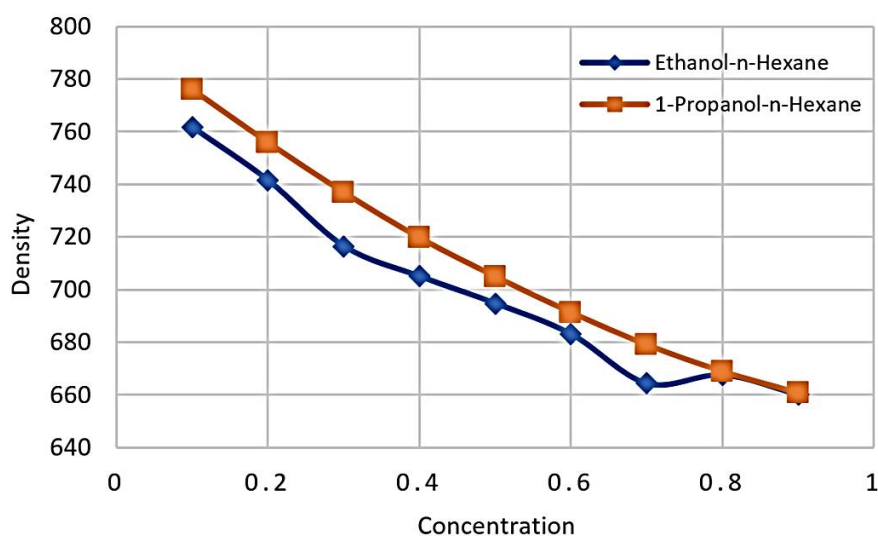


Figure 1. Density vs. n-hexane concentration in ethanol and 1-propanol at 298.15 K.

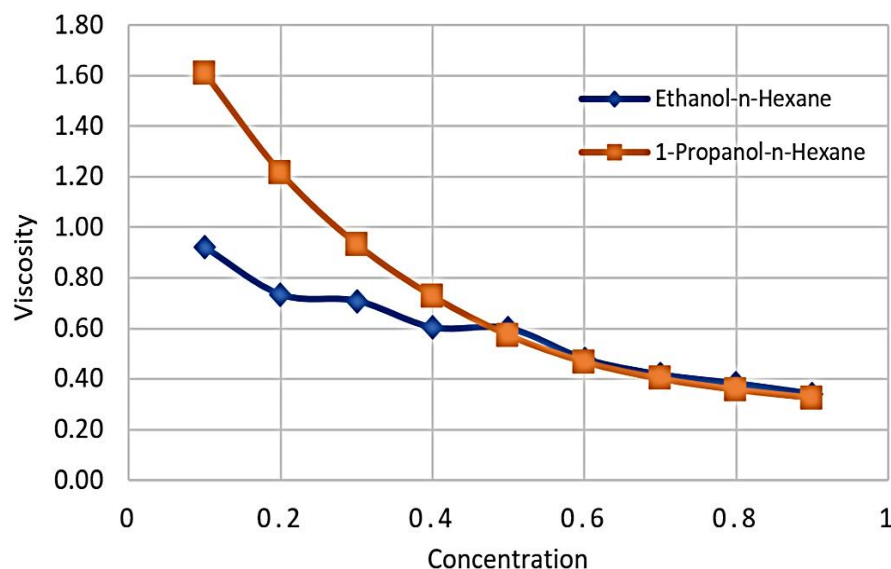


Figure 2. Viscosity vs. n-hexane concentration in ethanol and 1-propanol at 298.15 K.

Figure 4 shows that the isentropic compressibility of the 1-propanol–n-hexane system is lower than that of the ethanol–n-hexane system. Since compressibility is inversely related to the degree of molecular packing, the reduced values observed for 1-propanol–n-hexane suggest stronger packing compared to ethanol–n-hexane. This can be attributed to the higher solubility of n-hexane in 1-propanol, which promotes closer molecular association and results in decreased compressibility.

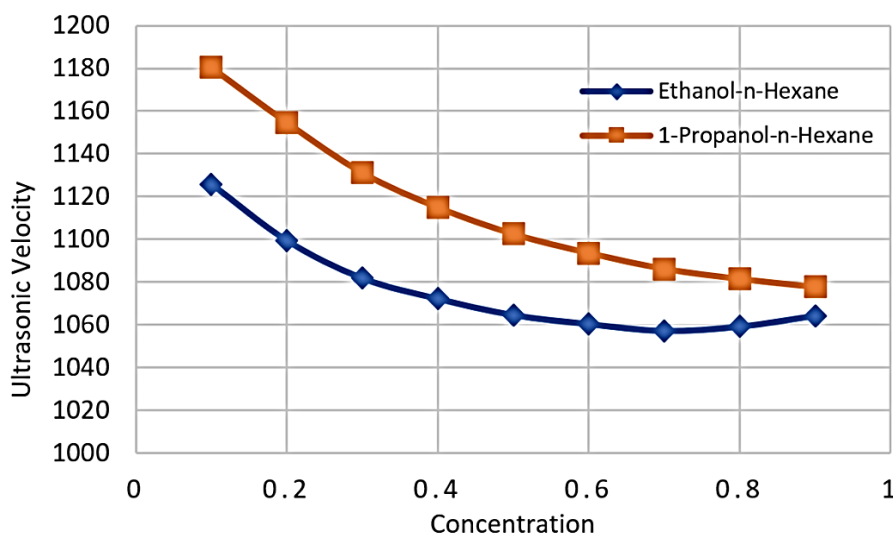


Figure 3. Ultrasonic velocity vs. n-hexane concentration in ethanol and 1-propanol at 298.15 K.

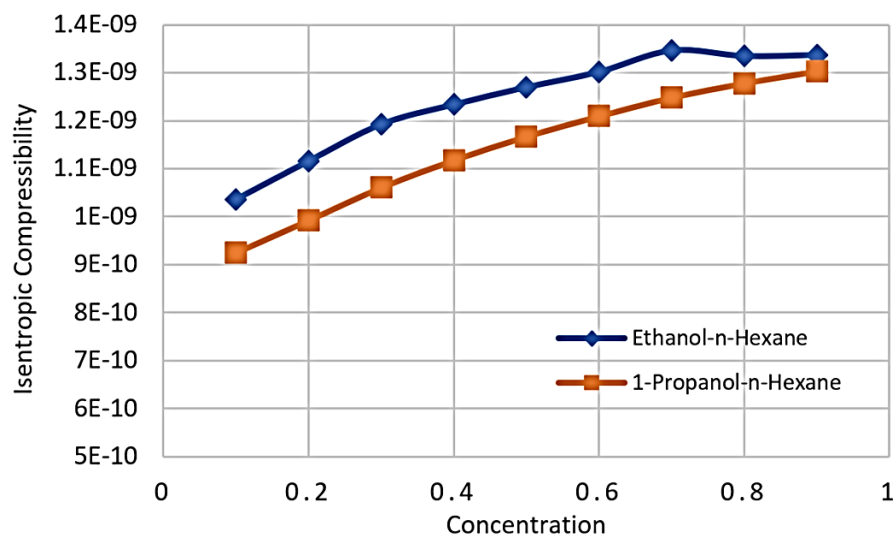


Figure 4. Isentropic compressibility vs n-hexane concentration in ethanol and 1-propanol at 298.15 K.

Figure 5 shows that acoustic impedance exhibits an opposite trend to isentropic compressibility, while Figure 6 indicates that the variation in free length for both systems follows the same trend as compressibility. Since these parameters are strongly influenced by molecular packing, the results suggest that the degree of close packing is greater in the 1-propanol–n-hexane system than in the ethanol–n-hexane system. This enhanced packing can be attributed to the higher solubility of n-hexane in 1-propanol, which increases the number of interacting molecules per unit volume and reduces the free space within the mixture [32–39].

Figure 7 shows that the free volume of the ethanol–n-hexane system is slightly lower than that of the 1-propanol–n-hexane system at mole fractions above 0.4. Since free volume depends on the number of molecules accommodated within a given volume, the smaller molecular size of ethanol compared to 1-propanol reduces the space requirement, thereby resulting in lower free volume values for ethanol–n-hexane mixtures [40, 41].

Similarly, Figure 8 indicates that the internal pressure of ethanol–n-hexane is marginally higher than that of the 1-propanol–n-hexane system. This effect can be attributed to stronger solute–solvent interactions in the ethanol-based mixtures, which arise due to the smaller size of ethanol molecules and

their closer approach to n-hexane. The enhanced interactions lead to a slight increase in internal pressure relative to the 1-propanol–n-hexane system [42, 43].

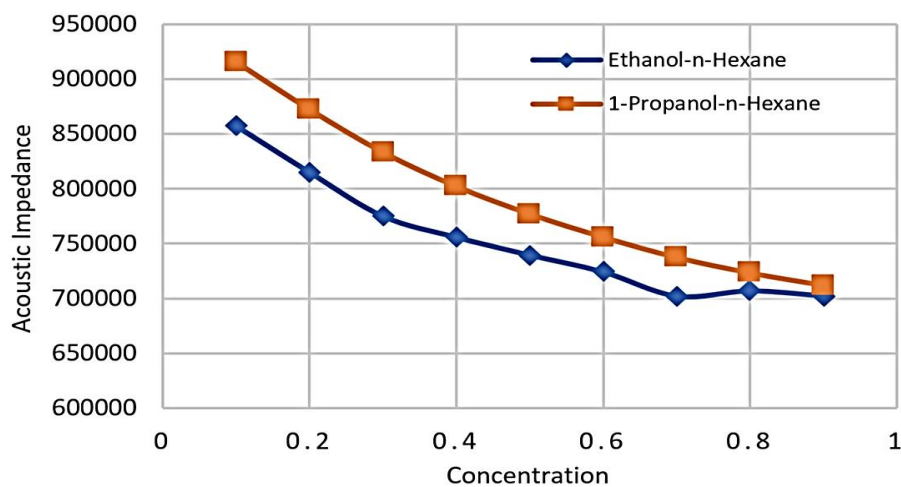


Figure 5. Acoustic impedance vs. n-hexane concentration in ethanol and 1-propanol at 298.15 K.

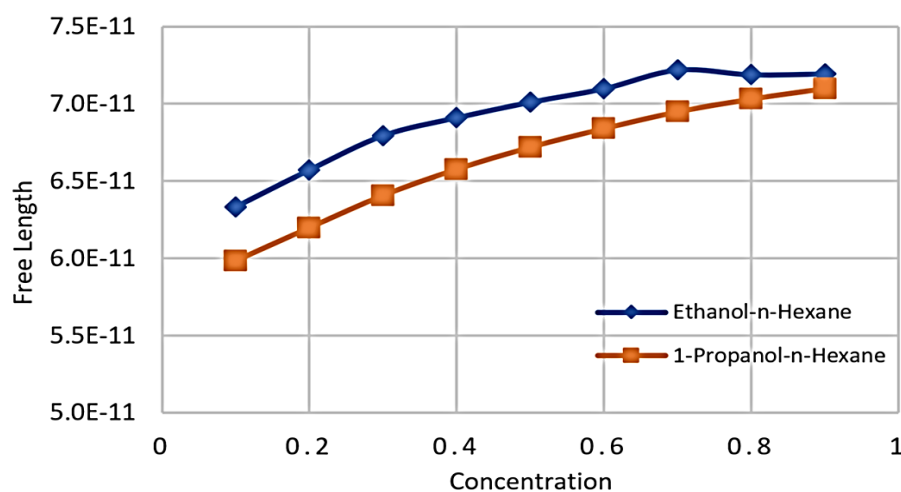


Figure 6. Free length vs. n-hexane concentration in ethanol and 1-propanol at 298.15 K.

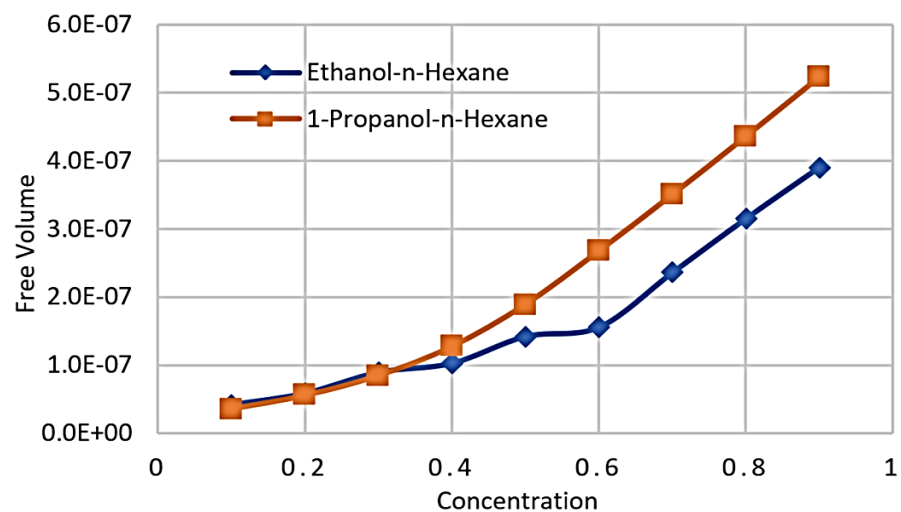


Figure 7. Free volume vs. n-hexane concentration in ethanol and 1-propanol at 298.15 K.

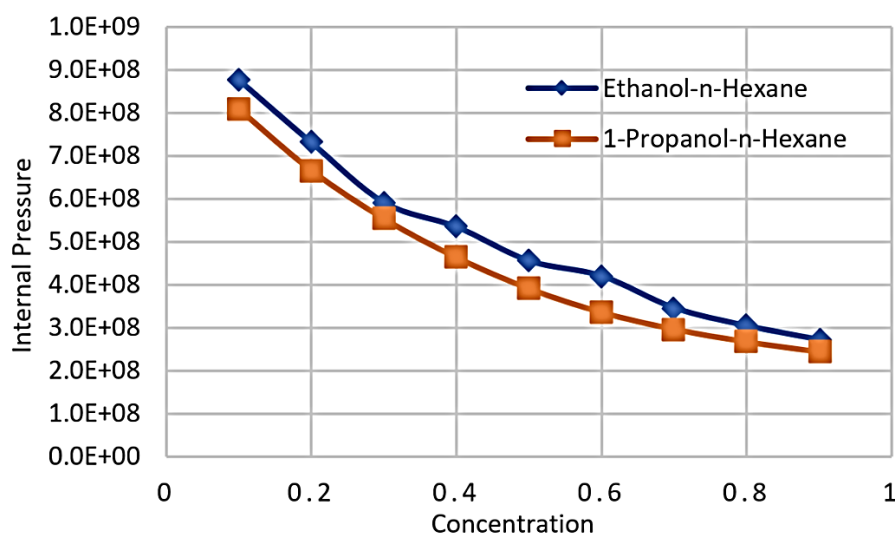


Figure 8. Internal pressure vs. n-hexane concentration in ethanol and 1-propanol at 298.15 K.

CONCLUSIONS

A comparative analysis of the ethanol–n-hexane and 1-propanol–n-hexane systems reveals that the longer carbon chain of 1-propanol enhances the solubility of n-hexane, leading to a higher density in the 1-propanol–based mixture. The greater polarizability of 1-propanol further contributes to increased viscosity, although at higher mole fractions of n-hexane, the difference becomes negligible due to the dominant influence of the nonpolar solvent. The elevated density of the 1-propanol–n-hexane system also corresponds to a higher ultrasonic velocity.

Examination of acoustic parameters, including isentropic compressibility, acoustic impedance, and free length, confirms a greater degree of molecular packing in the 1-propanol–n-hexane system, consistent with the enhanced solubility of n-hexane in 1-propanol compared to ethanol. In contrast, the smaller molecular size of ethanol results in a lower free volume in ethanol–n-hexane mixtures, as less space is required for molecular accommodation. Internal pressure values for both systems are nearly identical, suggesting comparable solute–solvent interactions overall.

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