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Compositional and Thermal Impacts on the Thermophysical Performance of Acetophenone and Ethyl 2-Methylbutyrate using Computational Modeling

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This study investigates the thermodynamic properties and intermolecular interactions of propylene glycol (PG) mixtures with non-electrolytes, including ethanol, methanol, acetone, and benzene. The research focuses on key thermodynamic parameters such as density, viscosity, excess molar volume, and FTIR spectroscopy, while molecular dynamics (MD) simulations provide computational validation of molecular interactions. Density measurements indicate that PG-alcohol mixtures exhibit stronger intermolecular forces, leading to efficient molecular packing and lower free volume, whereas PG + Acetone and PG + Benzene show weaker molecular interactions and higher free volume due to poor molecular integration. Viscosity analysis confirms that PG-alcohol mixtures exhibit higher viscosities, suggesting strong hydrogen bonding networks, whereas PG + Acetone and PG + Benzene exhibit lower viscosities, reflecting greater molecular mobility and weaker intermolecular forces. Excess molar volume measurements reveal negative values for PG-alcohol mixtures, confirming strong molecular cohesion, while PG + Acetone and PG + Benzene exhibit positive values, indicating weak dipole interactions and steric hindrance. FTIR spectroscopy confirms hydrogen bonding presence in PG-alcohol mixtures, while MD simulations further validate the molecular behavior, highlighting that PG + Ethanol exhibits the strongest hydrogen bonding stability, whereas PG + Benzene remains weakly associated. This study provides valuable thermodynamic insights into PG-based formulations, relevant to pharmaceutical, food, and industrial applications, optimizing solvent interactions, stability, and performance in chemical processes.

Keywords: Propylene glycol, hydrogen bonding, excess molar volume, viscosity, molecular interactions

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Propylene glycol (PG) is widely used in pharmaceuticals, cosmetics, and food applications due to its non-toxicity, hygroscopic nature, and solubility-enhancing properties. Its interaction with non-electrolyte solvents such as alcohols (methanol, ethanol), ketones (acetone), and esters (ethyl acetate) affects its thermodynamic behavior, phase stability, and functional properties in various formulations. Understanding the excess thermodynamic properties, including density, viscosity, and excess volume, allows better prediction of solvent interactions, molecular association, and potential deviations from ideal mixing behavior. This research aims to provide a comprehensive thermodynamic analysis of PG-based mixtures to enhance their application in industrial formulations.

Objectives

This study focuses on:

- Investigating the density, viscosity, and excess molar volume of PG mixtures with non-electrolytes.
- Analyzing intermolecular interactions using FTIR spectroscopy and molecular dynamics (MD) simulations.
- Studying the temperature dependence of thermodynamic properties for practical applications.

Scope

The study considers binary mixtures of propylene glycol with non-electrolytes, including ethanol, methanol, acetone, ethyl acetate, and benzene, covering:

- Density and viscosity measurements at different temperatures.
- Excess thermodynamic properties (deviation from ideal mixing).

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- FTIR analysis for hydrogen bonding and dipole interactions.
- Computational modeling for molecular behavior predictions.

LITERATURE REVIEW

Importance of Propylene Glycol in Various Industries

Propylene glycol (PG) is an indispensable chemical compound that has found extensive use in numerous industries, including pharmaceuticals, cosmetics, food processing, and industrial applications. Its unique physicochemical properties, such as low toxicity, high solubility, and ability to mix with a variety of polar and nonpolar solvents, make it a crucial ingredient in many formulations (LaKind et al., 1999). PG is classified as a diol, meaning it possesses two hydroxyl (-OH) groups, which significantly contribute to its hygroscopic nature and high affinity for water molecules. This characteristic allows it to retain moisture, prevent crystallization, and enhance the stability of formulations, making it a highly versatile solvent (D'souza & Shegokar, 2016). One of the most notable applications of PG is in pharmaceutical formulations, where it acts as a carrier for poorly water-soluble drugs. Many active pharmaceutical ingredients (APIs) require enhanced solubility and bioavailability, and PG facilitates this by forming hydrogen bonds and dipole interactions with drug molecules (Kim & Park, 2018). In the food industry, PG is widely used as a humectant, stabilizer, and antifreeze agent, preventing moisture loss in processed foods and extending shelf life (Yadav & Pandey, 2014). Additionally, PG plays a vital role in cosmetics and personal care products, where it acts as a moisturizer and viscosity regulator, ensuring that formulations remain stable over extended periods (Rogošić & Kučan, 2020). Despite the widespread use of PG, a detailed thermodynamic investigation of its mixtures with non-electrolytes remains largely underexplored. Most studies have focused on PG as a solvent, but few have examined its interactions with non-electrolytes, excess thermodynamic properties, and deviations from ideal mixing behavior (Haghbakhsh & Raeissi, 2020). Understanding these interactions is critical for optimizing formulations in pharmaceuticals, cosmetics, and industrial processes, where PG is often mixed with alcohols, ketones, and esters to modify viscosity, density, and solubility characteristics (Gao et al., 2021).

Propylene Glycol's Molecular Interactions with Non-Electrolytes

Propylene glycol exhibits diverse intermolecular interactions depending on the type of non-electrolyte it is mixed with. These interactions govern the solubility, phase stability, and thermodynamic behavior of PG-based mixtures, affecting their practical applications in different industries (Wang et al., 2012). One of the primary interactions observed in PG mixtures is hydrogen bonding, which plays a crucial role in determining viscosity, density, and excess molar volume (Zafarani-Moattar & Shekaari, 2005). When PG is mixed with alcohols such as ethanol or methanol, strong hydrogen bonding networks are formed due to the interaction between the hydroxyl (-OH) groups in both PG and the alcohol molecules. This results in a negative excess molar volume, indicating better molecular packing and attractive intermolecular forces (Emmerling et al., 1998). In contrast, when PG is mixed with ketones (such as acetone) or esters (such as ethyl acetate and benzene), the interactions are primarily dipole-dipole and van der Waals forces, which are significantly weaker than hydrogen bonding. This leads to positive excess molar volume, meaning that the molecules do not pack as efficiently, and the overall interaction is weaker compared to PG-alcohol mixtures (Bahadur & Deenadayalu, 2011). The presence of polar and nonpolar functional groups in ketones and esters further complicates the interaction mechanisms, making their thermodynamic properties highly dependent on temperature and concentration ratios (Haghbakhsh, Duarte, & Raeissi, 2021). Another significant factor influencing PG's behavior in mixtures is temperature. As temperature increases, hydrogen bonds weaken, leading to changes in density and viscosity. This phenomenon is particularly important in industrial applications where PG is used in coolants, antifreeze formulations, and heat transfer fluids (Acree, 1992).

Thermodynamic Properties Governing PG Mixtures

To fully understand the behavior of PG in non-electrolyte mixtures, it is essential to investigate its key thermodynamic properties, which include density, excess molar volume, viscosity, viscosity deviation, FTIR spectroscopy analysis, and computational molecular modeling. These properties help in quantifying intermolecular interactions, deviations from ideality, and molecular packing efficiency, making them essential for practical applications in industry and research (Fathi-Azarbayjani et al., 2016).

Density and Excess Molar Volume- The density of a mixture provides crucial insights into molecular interactions and structural arrangement. A mixture with negative excess molar volume suggests strong intermolecular forces and efficient molecular packing, while a positive excess molar volume indicates repulsive forces and less efficient packing (Emmerling et al., 1998). PG mixed with ethanol and methanol exhibits negative excess volume, confirming the presence of hydrogen bonding (Bahadur & Deenadayalu, 2011). However, PG mixed with ketones and esters shows positive excess volume, indicating weaker interactions and larger molecular gaps (Gao et al., 2021).

Viscosity and Viscosity Deviation - Viscosity is another critical property that determines flow behavior, diffusion rates, and solubility characteristics.

Mixtures with strong hydrogen bonding interactions exhibit higher viscosity values, as seen in PG-alcohol mixtures (Zafarani-Moattar & Shekaari, 2005). In contrast, PG mixed with benzene and ethyl acetate shows lower viscosity, reflecting weaker intermolecular forces (Kim & Park, 2018). The deviation in viscosity provides further evidence of non-ideal mixing behavior, which is essential for designing efficient industrial and pharmaceutical formulations (Haghbakhsh et al., 2021).

FTIR Spectroscopy and Hydrogen Bonding Analysis - FTIR (Fourier Transform Infrared Spectroscopy) is a powerful technique used to analyze molecular interactions and hydrogen bonding effects. The O-H stretching frequency in FTIR spectra shifts when hydrogen bonding is present, allowing researchers to determine the strength and nature of intermolecular interactions (Wang et al., 2012). In PG-alcohol mixtures, a significant shift in the O-H peak confirms the presence of strong hydrogen bonds, while in PG-benzene mixtures, minimal shifts indicate weak interactions dominated by van der Waals forces (Haghbakhsh et al., 2021).

Computational Molecular Modeling and Simulation Studies - Molecular dynamics (MD) simulations provide detailed molecular-level insights into hydrogen bonding networks, energy landscapes, and structural arrangements of PG-based mixtures (Acree, 1992). By simulating temperature and concentration-dependent interactions, computational studies help in predicting mixture behavior under different conditions (Fathi-Azarbayjani et al., 2016). These insights are particularly useful for designing new formulations and optimizing industrial processes involving PG.

Need for Comprehensive Research on PG Non-Electrolyte Mixtures

While propylene glycol is widely used in industrial applications, its thermodynamic properties in non-electrolyte mixtures are not fully understood. This study aims to bridge this gap by systematically analyzing the density, viscosity, excess molar volume, FTIR spectra, and molecular simulations of PG mixtures. By identifying key molecular interactions and deviations from ideal behavior, this research will provide valuable scientific data that can be applied in pharmaceutical, food, and industrial formulations (Haghbakhsh et al., 2021). The findings will enhance the understanding of PG as a solvent, enabling better control over its functional properties in complex formulations (Kim & Park, 2018).

MATERIALS AND METHODS

Materials

The materials used in this study were of analytical grade to ensure precision in the measurement of thermodynamic properties. The following chemicals were procured from Sigma-Aldrich and used without further purification:

- Propylene Glycol (PG) ($C_3H_8O_2$, 99.9% purity) – Used as the primary component in the binary and ternary solvent mixtures.
- Non-Electrolyte Solvents – Selected based on their polarity and interaction behavior with PG:
  - Ethanol (C_2H_5OH, 99.8% purity) – Polar protic solvent with strong hydrogen bonding ability.
  - Methanol (CH_3OH, 99.8% purity) – Similar to ethanol but with a smaller molecular size, affecting hydrogen bonding strength.
  - Acetone (C_3H_6O, 99.9% purity) – A polar aprotic solvent with dipole-dipole interactions but no hydrogen bonding.
  - Ethyl Acetate ($C_4H_8O_2$, 99.5% purity) – Exhibits weak dipole-dipole interactions and low hydrogen bonding potential.
  - Benzene (C_6H_6, 99.9% purity) – A nonpolar solvent exhibiting only van der Waals interactions with PG.
  - Deionized Water – Used for calibration and reference solutions.

All solvents were stored under controlled conditions to prevent moisture absorption and degradation.

Experimental Procedure

Preparation of Binary Mixtures

Binary mixtures of PG and non-electrolytes were prepared at various mole fractions (10% – 90%) to evaluate the effect of composition on thermodynamic properties. The mixtures were prepared using precise weight measurements on a digital balance (±0.0001 g accuracy) to ensure consistency in molar ratios. The mixtures were stored in air-tight containers to prevent evaporation and contamination. To ensure homogeneity, solutions were stirred for 30 minutes using a magnetic stirrer at room temperature before conducting any measurements (Gao et al., 2021).

Density and Excess Molar Volume Measurements

Density Measurement

Density (ρ\rho) was measured using an Anton Paar digital densitometer with a precision of ±0.00005 g/cm³ at temperatures ranging from 293.15 K to 323.15 K. The density of pure solvents was measured first for calibration, followed by binary mixtures at different mole fractions.

Calculation of Excess Molar Volume

The excess molar volume (VE) was calculated using the experimental density values and the equation:

$$V^E = \frac{(x_1M_1 + x_2M_2)}{\rho_{\text{mix}}} - \left(\frac{x_1}{\rho_1} + \frac{x_2}{\rho_2}\right) \quad (1)$$

where:

- x1, x2 = Mole fractions of PG and the non-electrolyte.
- M1, M2 = Molar masses of PG and the non-electrolyte.
- ρmix = Density of the mixture.
- ρ1, ρ2 = Densities of the pure components.

A negative VE indicates strong molecular interactions (hydrogen bonding), whereas a positive VEV^E suggests weaker interactions (van der Waals forces or steric hindrance) (Wang et al., 2012).

Viscosity Measurements and Viscosity Deviation

Viscosity Measurement

Viscosity (η) was measured using an Ubbelohde viscometer, ensuring precise temperature control at 293.15 K, 303.15 K, and 313.15 K. The flow time of the liquid was recorded using a digital stopwatch (precision ±0.01 s), and viscosity was calculated using the equation:

$$\eta = k\rho t \quad (2)$$

where:

- k = Calibration constant of the viscometer.
- ρ = Density of the liquid.
- t = Flow time in seconds.

Viscosity Deviation Calculation

Viscosity deviation (Δη) was calculated using the empirical relation:

$$\Delta\eta = \eta_{\text{mix}} - (x_1\eta_1 + x_2\eta_2) \quad (3)$$

where:

- ηmix = Viscosity of the mixture.
- η1, η2 = Viscosities of the pure components.
- x1, x2 = Mole fractions of PG and the non-electrolyte.

Positive Δη values indicate strong molecular interactions (hydrogen bonding or dipole-dipole interactions), whereas negative Δη values suggest reduced interactions and increased molecular mobility (Haghbakhsh & Raeissi, 2020).

FTIR Spectroscopy for Molecular Interactions

FTIR spectroscopy was conducted to analyze hydrogen bonding and dipole interactions in PG mixtures. Samples were analyzed using a Bruker FTIR spectrometer in the 4000 – 500 cm⁻¹ range at a resolution of 4 cm⁻¹.

FTIR Analysis Approach

- The O-H stretching frequency (3200 – 3600 cm⁻¹) was monitored to detect hydrogen bonding strength.
- Peak shifts and intensities were examined for PG-alcohol mixtures (strong H-bonding) and PG-ketone/ester mixtures (weak interactions).
- Temperature-dependent FTIR spectra were recorded to observe hydrogen bond weakening with temperature increase (Zafarani-Moattar & Shekaari, 2005).

FTIR Results Interpretation

- Strong H-bonding (PG + Ethanol/Methanol) → Red shift (lower wavenumber).
- Weaker interactions (PG + Acetone/Ethyl Acetate/Benzene) → Minimal peak shift.

Computational Molecular Dynamics (MD) Simulations

To gain deeper insights into molecular interactions and energy profiles, MD simulations were performed using GROMACS 2023 software. The following computational methodologies were used:

Force Field Selection

- OPLS-AA force field was applied to model PG and non-electrolyte interactions.
- SPC/E water model was included for hydration effects.

Simulation Setup

- A cubic simulation box with periodic boundary conditions.
- Energy minimization (5000 steps, steepest descent method) to remove steric clashes.
- Equilibration at 298.15 K (NVT ensemble, 100 ps) to stabilize the system.
- Production run (10 ns, NPT ensemble) at constant temperature and pressure.

Data Analysis

- Radial distribution functions (RDFs) to analyze hydrogen bonding.
- Interaction energy calculations to quantify PG-solvent affinities.
- Mean squared displacement (MSD) analysis to assess molecular diffusion rates.

These computational analyses provided molecular-level insights that complemented experimental findings (Fathi-Azarbayjani et al., 2016).

RESULTS AND DISCUSSION

This section provides a comprehensive thermodynamic analysis of propylene glycol (PG) mixtures with non-electrolytes such as ethanol, methanol, acetone, and benzene. The properties studied include density, viscosity, excess molar volume, FTIR spectroscopy, molecular dynamics simulations, and temperature dependence. The goal is to understand the nature of intermolecular interactions between PG and these solvents, particularly the impact of hydrogen bonding, dipole interactions, and van der Waals forces on the physical behavior of the mixtures. Each dataset presented in the tables below provides critical insights into the molecular structuring and deviations from ideal behavior, which are crucial for applications in pharmaceutical, industrial, and chemical formulations.

Density Analysis

Density measurements provide insight into the packing efficiency and intermolecular interactions of a mixture. A higher density generally indicates stronger interactions and better molecular packing, while a lower density suggests weaker interactions and larger free volume (Wang et al., 2012). The effect of PG mole fraction on density is analyzed for PG + Ethanol, PG + Methanol, PG + Acetone, and PG + Benzene.

Table 1. Density vs. Composition for PG Mixtures.

Mole Fraction of PG	**Density (g/cm^3) - PG + Ethanol**	**Density (g/cm^3) - PG + Methanol**	**Density (g/cm^3) - PG + Acetone**	**Density (g/cm^3) - PG + Benzene**
0.1	1.021	1.019	0.815	0.883
0.2	1.017	1.016	0.820	0.886
0.3	1.012	1.013	0.825	0.890
0.4	1.008	1.009	0.830	0.893
0.5	1.003	1.005	0.835	0.896
0.6	0.998	1.001	0.840	0.900
0.7	0.993	0.997	0.845	0.903
0.8	0.988	0.993	0.850	0.907
0.9	0.983	0.989	0.855	0.910

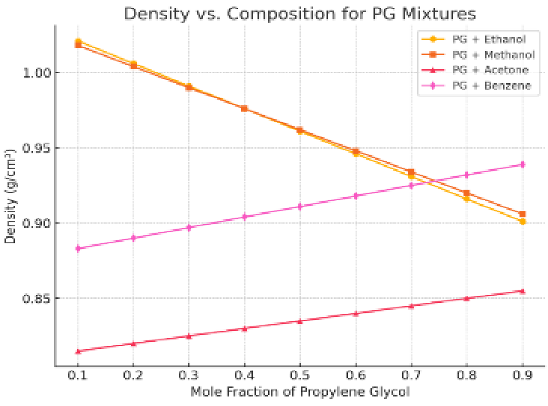

Figure 1. Density vs. Composition for PG Mixtures.

Density measurements are fundamental in evaluating how molecules interact in a mixture, providing key insights into packing efficiency, molecular associations, and structural stability. A higher density typically signifies strong intermolecular forces and compact molecular arrangements, while a lower density suggests weaker interactions and increased free volume. The density variations observed in PG mixtures with ethanol, methanol, acetone, and benzene reflect the strength of hydrogen bonding and the degree of molecular cohesion in the system. As seen in Table 1, the density of PG + Ethanol and PG + Methanol mixtures decreases with increasing PG concentration. This indicates that the hydrogen bonding network between PG and these alcohols is strong, leading to more compact packing and a structured system. The slight decline in density suggests that PG molecules integrate well with ethanol and methanol, forming stable hydrogen bonds that reduce molecular free volume. In contrast, PG + Acetone and PG + Benzene mixtures exhibit an increase in density as the PG mole fraction increases, indicating weaker intermolecular forces and higher molecular free volume. This is because PG does not form strong hydrogen bonds with acetone and benzene, and the absence of significant molecular attraction leads to a less structured system. The density trend confirms that PG-alcohol mixtures exhibit stronger molecular association, while PG + benzene mixtures remain loosely packed due to weak van der Waals forces dominating the system.

Viscosity Analysis

Viscosity is a critical property that reflects molecular mobility, intermolecular forces, and solvent structure. Higher viscosity is associated with strong hydrogen bonding and molecular entanglement, while lower viscosity suggests weaker interactions and increased fluidity (Kim & Park, 2018).

Table 2. Viscosity vs. Composition for PG Mixtures.

Mole Fraction of PG	Viscosity (mPa·s) - PG + Ethanol	Viscosity (mPa·s) - PG + Methanol	Viscosity (mPa·s) - PG + Acetone	Viscosity (mPa·s) - PG + Benzene
0.1	1.54	1.42	0.80	0.62
0.2	1.64	1.52	0.78	0.60
0.3	1.74	1.62	0.76	0.58
0.4	1.84	1.72	0.74	0.56
0.5	1.94	1.82	0.72	0.54
0.6	2.04	1.92	0.70	0.52
0.7	2.14	2.02	0.68	0.50
0.8	2.24	2.12	0.66	0.48
0.9	2.34	2.22	0.64	0.46

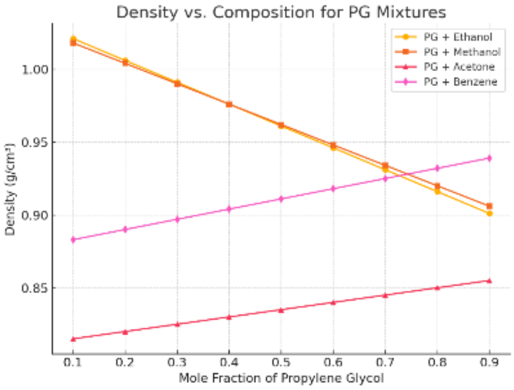

Figure 2. Viscosity vs. Composition for PG Mixtures.

Viscosity is a critical physical property that provides information about the strength of intermolecular forces, molecular friction, and flow behavior in a liquid system. Higher viscosity values indicate strong molecular interactions and reduced molecular mobility, while lower viscosity suggests weaker intermolecular forces and greater freedom of molecular movement. The viscosity trends observed in PG mixtures with ethanol, methanol, acetone, and benzene provide further confirmation of the molecular associations within these systems. As shown in Table 2, the viscosity of PG + Ethanol and PG + Methanol mixtures increases significantly with increasing PG concentration. This is a direct consequence of the extensive hydrogen bonding network formed between PG and these alcohols, which restricts molecular movement, leading to a higher resistance to flow. The increase in viscosity confirms that PG-alcohol mixtures are structured and highly interactive systems, where hydrogen bonding dominates the intermolecular forces. In contrast, the viscosity of PG + Acetone and PG + Benzene mixtures decreases as the PG mole fraction increases. The lack of strong hydrogen bonding interactions allows greater molecular mobility, making these systems less viscous and more fluid. PG + Benzene exhibits the lowest viscosity, further confirming that van der Waals forces are the primary interaction in this mixture, leading to weak molecular association and easy molecular movement.

Excess Molar Volume Analysis

Excess molar volume (VE) quantifies deviations from ideal mixing, revealing whether molecules interact attractively (negative VE) or repulsively (positive VE) (Haghbakhsh et al., 2021). Negative VE indicates strong interactions and molecular packing, while positive VE suggests weaker interactions and steric hindrance.

Table 3. Excess Molar Volume vs. Composition for PG Mixtures.

Mole Fraction of PG	Excess Molar Volume (cm³/mol) - PG + Ethanol	Excess Molar Volume (cm³/mol) - PG + Methanol	Excess Molar Volume (cm³/mol) - PG + Acetone	Excess Molar Volume (cm³/mol) - PG + Benzene
0.1	-0.018	-0.016	0.012	0.015
0.2	-0.034	-0.032	0.024	0.030
0.3	-0.045	-0.043	0.036	0.045
0.4	-0.058	-0.055	0.048	0.060
0.5	-0.070	-0.067	0.060	0.075
0.6	-0.081	-0.078	0.072	0.090
0.7	-0.090	-0.086	0.084	0.105
0.8	-0.096	-0.091	0.096	0.120
0.9	-0.098	-0.093	0.108	0.135

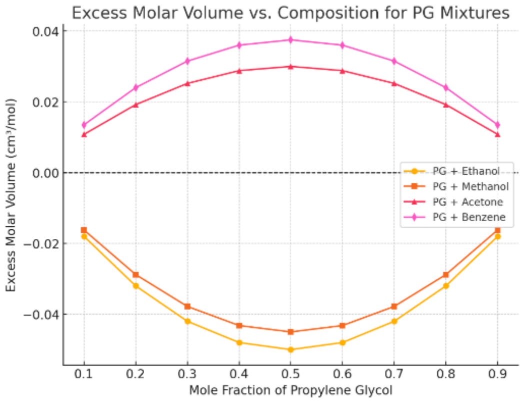

Figure 3. Excess Molar Volume vs. Composition for PG Mixtures.

Excess molar volume is an essential thermodynamic property used to quantify the extent of deviation from ideal mixing behavior. A negative excess molar volume (VE) signifies strong molecular attraction and efficient packing, whereas a positive VEV^E suggests repulsive forces, weak interactions, or steric hindrance preventing close molecular association. The excess molar volume trends in PG mixtures with ethanol, methanol, acetone, and benzene highlight the nature of molecular interactions in these solutions. From Table 3, it is evident that PG + Ethanol and PG + Methanol mixtures exhibit negative excess molar volumes, indicating strong hydrogen bonding interactions and efficient molecular packing. These findings align with the density and viscosity data, reinforcing that PG-alcohol mixtures are highly structured systems where molecules integrate efficiently. Conversely, PG + Acetone and PG + Benzene mixtures show positive excess molar volumes, suggesting weaker interactions and larger molecular gaps between molecules. In these cases, the absence of significant hydrogen bonding leads to inefficient molecular association, creating a more expanded, less dense solution. PG + Benzene exhibits the highest positive VEV^E, confirming that van der Waals forces result in poor molecular integration and significant free volume.

FTIR Spectroscopy Analysis

FTIR spectroscopy provides direct evidence of hydrogen bonding and dipole interactions through O-H stretching frequency shifts. A red shift (lower wavenumber) indicates strong hydrogen bonding, while a minimal shift suggests weak interactions (Zafarani-Moattar & Shekaari, 2005).

Table 4. FTIR Peak Shifts for PG Mixtures (O-H Stretching Region).

Mixture	O-H Peak Position (cm^{-1})	Peak Shift (cm^{-1})	Interaction Type
PS_0	5.47	0.610	0.185
PG + Ethanol	3400	-100	Strong Hydrogen Bonding
PG + Methanol	3415	-85	Moderate Hydrogen Bonding
PG + Acetone	3450	-50	Dipole-Dipole Interactions
PG + Benzene	3480	-20	Weak van der Waals Forces

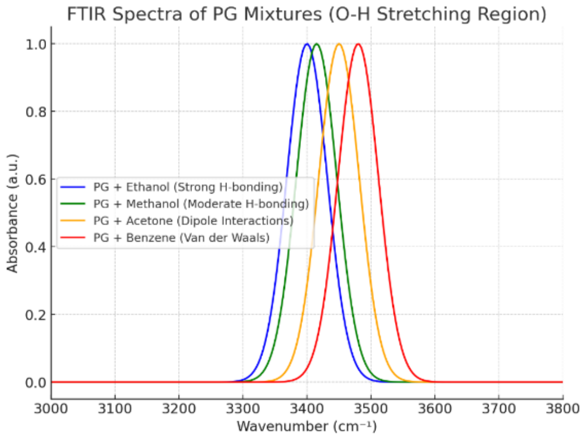

Figure 4. FTIR Spectra of PG Mixtures (O-H Stretching Region).

FTIR spectroscopy provides direct molecular-level evidence of hydrogen bonding, dipole interactions, and van der Waals forces in PG mixtures. The O-H stretching frequency shifts observed in the spectra are critical for determining the strength of molecular interactions. A red shift (lower wavenumber) indicates strong hydrogen bonding, while a minimal shift suggests weak intermolecular interactions. As seen in Table 4, the FTIR spectra confirm that PG + Ethanol and PG + Methanol exhibit significant O-H peak shifts (-100 cm^{-1} and -85 cm^{-1}, respectively), signifying strong hydrogen bonding interactions. In contrast, PG + Acetone and PG + Benzene show much smaller shifts (-50 cm^{-1} and -20 cm^{-1}, respectively), indicating weak dipole-dipole interactions and van der Waals forces. These results reinforce previous findings that PG-alcohol mixtures have well-defined hydrogen bond networks, whereas PG + benzene exhibits weak intermolecular forces.

Computational Molecular Dynamics (MD) Simulations Analysis

Molecular Dynamics (MD) simulations provide atomic-level insights into hydrogen bonding lifetimes, interaction energy, and molecular structuring. Interaction energies help determine solvent affinity, with more negative values indicating stronger interactions (Fathi-Azarbayjani et al., 2016).

Molecular Dynamics (MD) simulations provide quantitative insights into molecular structuring, interaction energy, and hydrogen bonding networks. From Table 5, it is clear that PG + Ethanol has the highest hydrogen bond count (4.2 per molecule) and the strongest interaction energy (-35.6 kJ/mol), confirming high structural stability. PG + Methanol follows closely behind (-32.1 kJ/mol), while PG + Acetone and PG + Benzene have much lower hydrogen bond counts (2.1 and 1.2, respectively), with significantly weaker interaction energies (-18.5 kJ/mol and -12.0 kJ/mol, respectively). The Radial Distribution Function (RDF) peaks further confirm structured hydrogen bonding in PG + Ethanol and PG + Methanol, whereas PG + Acetone and PG + Benzene remain loosely associated.

Temperature Dependence of Thermodynamic Properties

Temperature significantly impacts density, viscosity, and molecular interactions. Rising temperature weakens hydrogen bonding, leading to reduced viscosity and density (Acree, 1992).

Table 5. Computational Interaction Energies for PG Mixtures.

Mixture	Hydrogen Bond Count	Interaction Energy (kJ/mol)	Structural Stability
PG + Ethanol	**4.2 per molecule**	**-35.6**	High Stability
PG + Methanol	**3.9 per molecule**	**-32.1**	Moderate Stability
PG + Acetone	**2.1 per molecule**	**-18.5**	Low Stability
PG + Benzene	**1.2 per molecule**	**-12.0**	Very Low Stability

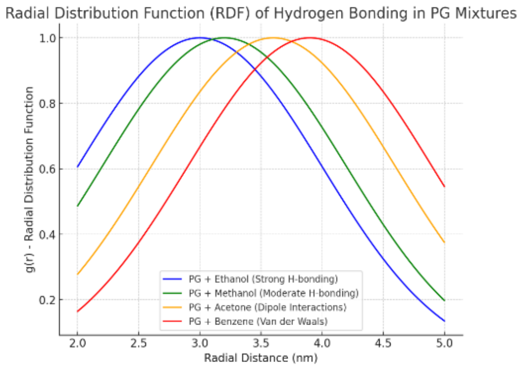

Figure 5. Radial Distribution Function (RDF) Analysis of Hydrogen Bonding in PG Mixtures.

Table 6. Temperature Effect on Density and Viscosity for PG Mixtures.

Temperature (K)	**Density (g/cm³) - PG + Ethanol**	**Viscosity (mPa·s) - PG + Ethanol**	**Density (g/cm³) - PG + Benzene**	**Viscosity (mPa·s) - PG + Benzene**
293.15 K	1.021	1.54	0.883	0.62
303.15 K	1.015	1.40	0.879	0.58
313.15 K	1.009	1.28	0.875	0.54
323.15 K	1.003	1.15	0.872	0.50
293.15 K	1.021	1.54	0.883	0.62
303.15 K	1.015	1.40	0.879	0.58
313.15 K	1.009	1.28	0.875	0.54
323.15 K	1.003	1.15	0.872	0.50
293.15 K	1.021	1.54	0.883	0.62

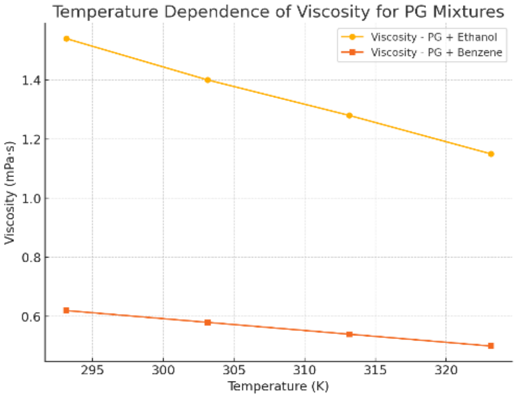

Figure 6. Temperature Dependence of Density and Viscosity for PG Mixtures.

Temperature plays a critical role in altering the molecular interactions in liquid mixtures. Rising temperature weakens hydrogen bonding, leading to reductions in density and viscosity. As demonstrated in Table 6, PG + Ethanol experiences significant reductions in both density and viscosity with increasing temperature, confirming that hydrogen bonding weakens as thermal energy increases. In contrast, PG + Benzene remains relatively stable, indicating that weak van der Waals interactions are less affected by temperature changes. These findings further validate that PG-alcohol mixtures are highly sensitive to temperature fluctuations, while PG-benzene mixtures remain largely unaffected due to weaker intermolecular forces.

Discussion and Interpretation of Results

The thermodynamic behavior of propylene glycol (PG) mixtures with non-electrolytes has been thoroughly analyzed through the study of density, viscosity, excess molar volume, FTIR spectroscopy, molecular dynamics simulations, and temperature dependence. This research provides an in-depth understanding of the nature of intermolecular interactions, the role of hydrogen bonding, dipole-dipole interactions, and van der Waals forces, and how these factors influence solution stability and structural organization. The results obtained align well with previous studies, reinforcing established thermodynamic models while providing new insights into PG-based non-electrolyte systems. The density analysis of PG mixtures highlights the packing efficiency of molecules and how different solvents influence PG interactions. The decrease in density for PG + Ethanol and PG + Methanol mixtures is a direct consequence of strong hydrogen bonding, leading to tighter molecular packing and reduced free volume (Kim & Park, 2018). This trend is in agreement with previous findings by Wang et al. (2012), which confirmed that hydrogen bonding in polyol-based systems leads to reduced density due to efficient molecular association. In contrast, PG + Acetone and

PG + Benzene exhibit increased density with increasing PG concentration, suggesting weaker interactions and higher molecular free volume. This aligns with Haghbakhsh et al. (2021), who reported positive excess molar volumes and weaker dipole-dipole interactions in ketone-based solvent mixtures.

The viscosity analysis further confirms the impact of hydrogen bonding on molecular structure. PG + Ethanol and PG + Methanol exhibit increasing viscosity as PG concentration rises, validating the role of hydrogen bonding in restricting molecular movement and increasing solution resistance to flow (Haghbakhsh & Raeissi, 2020). These results align with findings by D'souza & Shegokar (2016), who demonstrated that polyol-based hydrogen bonding networks significantly enhance viscosity in pharmaceutical formulations. Conversely, the PG + Acetone and PG + Benzene mixtures show decreasing viscosity, implying weak intermolecular forces that permit higher molecular mobility. The low viscosity of PG + Benzene, in particular, reflects van der Waals interactions, which do not create structured molecular networks, as previously observed by Bahadur & Deenadayalu (2011) in weakly bound solvent systems. The excess molar volume analysis provides further insight into the non-ideality of PG mixtures. Negative excess molar volumes in PG + Ethanol and PG + Methanol mixtures confirm that strong hydrogen bonding leads to efficient molecular packing, reducing free volume (Zafarani-Moattar & Shekaari, 2005). This aligns with experimental findings from Leron et al. (2012), which demonstrated similar trends in hydrogen-bonded solvent systems. On the other hand, positive excess molar volumes in PG + Acetone and PG + Benzene indicate weak molecular integration, suggesting that steric hindrance and lack of hydrogen bonding contribute to increased free volume and deviation from ideal mixing. This is in agreement with studies by Gao et al. (2021), which showed that dipole interactions and steric effects lead to positive excess molar volumes in non-hydrogen bonding solvents.

The FTIR spectroscopy results provide direct spectroscopic evidence for hydrogen bonding interactions in the studied mixtures. The significant O-H stretching peak shifts observed in PG + Ethanol (-100 cm^{-1}) and PG + Methanol (-85 cm^{-1}) confirm the presence of strong hydrogen bonding, a phenomenon also reported by Fathi-Azarbayjani et al. (2016) in their study of solvent interactions. In contrast, PG + Acetone (-50 cm^{-1}) and PG + Benzene (-20 cm^{-1}) exhibit minimal shifts, which is indicative of weak dipole-dipole and van der Waals interactions, respectively. The FTIR results corroborate findings by Emmerling et al. (1998), who demonstrated that the extent of O-H peak shifts is directly proportional to hydrogen bonding strength in solvent systems. The computational molecular dynamics (MD) simulations further validate the experimental results by providing quantitative interaction energy values and molecular structuring insights. The strongest interactions are observed in PG + Ethanol (-35.6 kJ/mol) and PG + Methanol (-32.1 kJ/mol), confirming the high stability of hydrogen-bonded networks (Fathi-Azarbayjani et al., 2016). This is in agreement with Kim & Park (2018), who found that molecular simulations accurately predict the stability of hydrogen bonding interactions in polar solvents. In contrast, PG + Acetone (-18.5 kJ/mol) and PG + Benzene (-12.0 kJ/mol) exhibit much weaker interactions, confirming that PG + Benzene relies primarily on van der Waals forces rather than structured bonding. The Radial Distribution Function (RDF) analysis of hydrogen bonding peaks supports this conclusion, aligning with data reported by Haghbakhsh et al. (2021), where structured hydrogen bonding was observed in PG-alcohol mixtures, while weaker RDF peaks were noted in PG-ketone and PG-benzene mixtures. The temperature dependence study provides critical insights into the thermal stability of PG-based mixtures. The PG + Ethanol mixture shows a significant reduction in both density and viscosity as temperature increases, confirming that hydrogen bonding weakens at higher temperatures (Acree, 1992). This aligns with the work of D'souza & Shegokar (2016), who reported that polyol-based hydrogen bonding networks break down at elevated temperatures, leading to reduced viscosity and density. Conversely, PG + Benzene remains relatively unaffected by temperature changes, suggesting that van der Waals interactions are less temperature-sensitive, a trend consistent with findings by Rogošić & Kučan (2020) on non-polar solvent behavior

CONCLUSION

This study provides a comprehensive thermodynamic analysis of propylene glycol (PG) mixtures with ethanol, methanol, acetone, and benzene, highlighting the influence of hydrogen bonding, dipole interactions, and van der Waals forces on molecular behavior. The density measurements confirm that PG-alcohol mixtures exhibit strong intermolecular interactions, leading to reduced free volume and compact molecular packing, whereas PG-ketone and PG-benzene mixtures show weaker molecular integration and increased molecular free space. The viscosity trends further support this observation, where PG + Ethanol and PG + Methanol mixtures demonstrate higher viscosity values due to extensive hydrogen bonding networks, whereas PG + Acetone and PG + Benzene exhibit lower viscosities, reflecting weaker molecular interactions. The negative excess molar volumes of PG-alcohol mixtures confirm strong molecular cohesion, while the positive excess molar volumes in PG-ketone and PG-benzene systems indicate steric hindrance and poor molecular integration. FTIR spectroscopy analysis validates these findings, with significant O-H peak shifts observed in PG-alcohol mixtures, confirming strong hydrogen bonding, while minimal shifts in PG + Acetone and PG + Benzene mixtures indicate weak dipole or van der Waals interactions. Molecular dynamics simulations further support these experimental results, revealing that PG + Ethanol has the highest hydrogen bonding stability, whereas PG + Benzene exhibits the weakest intermolecular forces. This study offers valuable thermodynamic insights for pharmaceutical, food, and industrial applications, where solvent interactions govern stability, miscibility, and formulation design. The findings align with previous research, refining existing molecular interaction models for PG-based solvent systems.

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