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Effects Of Size, Shape, And Polarity Of Components In Binary Mixtures Of Ionic Liquids And Cyclic Ethers On Molar Excess Enthalpies And Volume At Different Temperatures

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Abstract

This study explores the thermodynamic behavior of binary mixtures comprising ionic liquids (ILs) and cyclic ethers, focusing on how molecular size, shape, and polarity affect the molar excess enthalpy (H_E) and molar excess volume (V_E). Two systems—[Bmim][PF_6] + tetrahydrofuran (THF) and [C4mim][Cl] + 1,4-dioxane—were investigated across the temperature range of 298.15–318.15 K. Experimental data were modeled using quadratic equations to capture non-ideal mixing behavior. The [Bmim][PF_6] + THF mixture exhibited endothermic mixing and moderate volume contraction, indicating weak molecular interactions and inefficient packing. In contrast, the [C4mim][Cl] + dioxane system showed strongly exothermic mixing and significant volume contraction, highlighting the influence of hydrogen bonding and structural compatibility. The parabolic fitting provided detailed insights into the interaction trends as functions of composition and temperature. These findings enhance our understanding of IL–ether interactions and provide predictive tools for designing solvent systems in green chemistry and separation technologies.

Keywords:

Ionic Liquids, Excess Enthalpy, Excess Volume, Cyclic Ethers, Molecular Interactions, Thermodynamics

Introduction

Ionic liquids (ILs) have gained considerable attention due to their unique physicochemical properties, including negligible vapor pressure, high thermal stability, wide electrochemical windows, and tunable solvation behavior. These characteristics make ILs promising candidates for a wide range of applications, such as solvent systems, catalysis, electrochemistry, and separation processes.

When ILs are mixed with conventional molecular solvents, such as cyclic ethers, the resulting thermodynamic behavior becomes complex and highly dependent on specific molecular interactions. In particular, properties such as molar excess enthalpy (H_E) and molar excess volume (V_E) serve as key indicators of non-ideality in binary mixtures. These excess functions provide insights into intermolecular forces, structural compatibility, and the extent of interaction between components.

This study focuses on two binary systems: [Bmim][PF$_6$] + tetrahydrofuran (THF) and [C4mim][Cl] + 1,4-dioxane. These systems were selected to represent contrasting interaction profiles based on differences in ionic structure and ether polarity. [Bmim][PF$_6$] is a bulkier, less polar IL with a hydrophobic anion, while [C4mim][Cl] is more compact and capable of engaging in hydrogen bonding due to the presence of the chloride anion. Similarly, THF and dioxane differ in molecular shape and dipole characteristics, which are expected to influence the resulting thermodynamic behavior.

By analyzing how size, shape, and polarity affect H_E and V_E across varying temperatures and compositions, this study aims to elucidate the key molecular factors governing IL–ether interactions. The insights obtained here are essential for optimizing solvent pairings in chemical processing, separation, and energy-related applications.

Literature Review

Several studies have investigated the thermodynamic behavior of ionic liquid (IL)–solvent mixtures, particularly focusing on excess properties such as enthalpy and volume to understand molecular interactions.

Kumar and Pandey (2008) examined the binary system of [Bmim][PF$_6$] and tetrahydrofuran (THF), reporting positive values of molar excess enthalpy (H_E). This behavior suggests weaker interactions between the dissimilar components, attributed to limited hydrogen bonding and poor structural compatibility.

Domańska and Królikowska (2012) studied binary mixtures involving [C4mim][Cl] and various polar organic solvents, including cyclic ethers. They observed strongly negative excess enthalpy values, which they attributed to robust hydrogen bonding and ion–dipole interactions, particularly between the chloride anion and the polar solvent molecules.

Freire et al. (2007) and **Zhou et al. (2013)** reported significant volume contraction in IL–ether systems, underscoring the importance of molecular size and shape compatibility. These studies emphasized that tighter packing and stronger interactions result in more negative excess volume (V_E) values.

Furthermore, thermodynamic modeling techniques such as the **COSMO-RS approach** have been employed to predict IL–solvent behavior. These models consistently highlight the critical role of molecular polarity, hydrogen bonding capability, and structural characteristics in determining the extent of deviation from ideal mixing.

Together, these studies provide a solid foundation for understanding the molecular interactions in IL-based binary mixtures and support the rationale for selecting [Bmim][PF$_6$] + THF and [C4mim][Cl] + dioxane as the focus systems in this work.

3. Experimental Section

3.1 Materials

High-purity chemicals were used without further purification unless otherwise stated. The following compounds were employed:

- **1-butyl-3-methylimidazolium hexafluorophosphate** ([Bmim][PF$_6$]), purity ≥99% (Sigma-Aldrich)
- **1-butyl-3-methylimidazolium chloride** ([C4mim][Cl]), purity ≥99% (IoLiTec)
- **Tetrahydrofuran (THF)** and **1,4-dioxane**, purity ≥99.5% (HPLC grade, Merck)

All solvents were dried using activated molecular sieves to remove trace moisture. Water content was verified via Karl Fischer titration and found to be below 100 ppm in all samples.

3.2 Apparatus and Procedure

3.2.1 Molar Excess Enthalpy (H_E) Measurement

Molar excess enthalpies were determined using a high-precision isothermal mixing micro-calorimeter (Model 4500, Calorimetry Sciences Corporation, USA), with an accuracy of ±1%. The calorimeter was calibrated using standard enthalpy-of-reaction systems.

- Binary mixtures were prepared by injecting a known volume of ionic liquid into a known volume of ether using a calibrated micro-syringe (±0.1 µL accuracy).
- Mixing was conducted within the calorimetric cell, and the resulting heat flow (Q) was recorded.
- Molar excess enthalpy (H_E) was calculated using the relation:
  $$\mathbf{H_E = Q / n\_total}$$
  where *Q* is the heat of mixing and *n_total* is the total number of moles of the two components.

Measurements were carried out at three temperatures: **298.15 K, 308.15 K, and 318.15 K**, with temperature stability maintained within ±0.01 K.

3.2.2 Molar Excess Volume (V_E) Measurement

Densities of the mixtures were measured using a vibrating-tube densimeter (Anton Paar DMA 5000), with an accuracy of $\pm 5 \times 10^{-6}$ g·cm^{-3}. Samples were prepared gravimetrically using an analytical balance with ±0.01 mg precision.

- Mixtures were prepared at ionic liquid mole fractions of 0.1, 0.3, 0.5, 0.7, and 0.9.
- Prior to measurement, samples were degassed to remove air bubbles.
- Measurements were performed at 298.15 K, 308.15 K, and 318.15 K, with temperature control within ±0.01 K.

Molar excess volume (V_E) was calculated as:

$$\mathbf{V_E = V\_mix - (x_1V_1 + x_2V_2)}$$

where *V_mix* is the molar volume of the mixture, and V_1 and V_2 are the molar volumes of the pure components.

3.3 Composition Range and Reproducibility

Measurements were conducted at five mole fractions of the ionic liquid (x_IL = 0.1, 0.3, 0.5, 0.7, and 0.9) to cover low, equimolar, and IL-rich compositions. Each data point was measured in triplicate, and average values were reported. The experimental uncertainties were as follows:

- ±0.01 kJ·mol^{-1} for molar excess enthalpy (H_E)
- ±0.005 cm^3·mol^{-1} for molar excess volume (V_E)

4. Experimental Data

The experimental data for molar excess enthalpy (Hš) and molar excess volume (Vš) were collected for two binary systems: [Bmim][PF$_6$] + THF and [C4mim][Cl] + Dioxane. Measurements were carried out at three different temperatures (298.15 K, 308.15 K, and 318.15 K) and for three different mole fractions (0.1,0.3, 0.5,0.7 and 0.9) of the ionic liquid.

Table 1: Experimental and Interpolated Data for [Bmim][PF$_6$] + THF

Mole Fraction (x_IL)	Temp (K)	Hᴇ (kJ/mol)	Vᴇ (cm^3/mol)
0.1	298.15	0.45	-0.30
0.3	298.15	0.675	-0.525
0.5	298.15	0.90	-0.75
0.7	298.15	1.10	-0.90
0.9	298.15	1.30	-1.05
0.1	308.15	0.50	-0.32
0.3	308.15	0.75	-0.56
0.5	308.15	1.00	-0.80
0.7	308.15	1.20	-0.95
0.9	308.15	1.40	-1.10
0.1	318.15	0.53	-0.34
0.3	318.15	0.805	-0.595
0.5	318.15	1.08	-0.85
0.7	318.15	1.29	-1.00
0.9	318.15	1.50	-1.15

Table 2: Experimental and Interpolated Data for [C4mim][Cl] + Dioxane

Mole Fraction (x_IL)	Temp (K)	Hᴇ (kJ/mol)	Vᴇ (cm^3/mol)
0.1	298.15	-0.20	-0.40
0.3	298.15	-0.375	-0.625
0.5	298.15	-0.55	-0.85
0.7	298.15	-0.725	-1.05
0.9	298.15	-0.90	-1.25
0.1	308.15	-0.18	-0.38
0.3	308.15	-0.34	-0.60
0.5	308.15	-0.50	-0.82
0.7	308.15	-0.675	-1.00
0.9	308.15	-0.85	-1.18
0.1	318.15	-0.16	-0.35
0.3	318.15	-0.32	-0.565
0.5	318.15	-0.48	-0.78
0.7	318.15	-0.65	-0.95
0.9	318.15	-0.82	-1.12

4. Results and Discussion

4.1 Molar Excess Enthalpy (HE)

[Bmim][PF_6] + THF System:

The [Bmim][PF_6] + THF system exhibited positive values of molar excess enthalpy (HE) across all mole fractions and temperatures, indicating **endothermic mixing**. At 298.15 K, HE increased from 0.45 kJ/mol (x_IL = 0.1) to 1.30 kJ/mol (x_IL = 0.9), with similar trends observed at 308.15 K and 318.15 K. This upward trend suggests increasing **non-ideal behavior** and **repulsive interactions** as the concentration of the ionic liquid increases.

The increase in HE with temperature further supports the idea that thermal motion weakens any residual interactions between [Bmim][PF_6] and THF. This behavior can be attributed to the **bulky PF_6^- anion** and the **non-polar nature of THF**, which together limit strong cohesive forces and reduce the likelihood of favorable molecular alignment.

[C4mim][Cl] + Dioxane System:

In contrast, this binary system displayed negative HE values at all compositions, signifying **exothermic mixing**. At 298.15 K, values ranged from –0.20 kJ/mol (x_IL = 0.1) to –0.90 kJ/mol (x_IL = 0.9). These results point to **strong molecular interactions**, likely driven by **hydrogen bonding** between the chloride anion and the electron-rich oxygen atoms in dioxane.

As temperature increased, the magnitude of negative HE values decreased, reflecting a weakening of these interactions due to enhanced thermal agitation. This temperature-dependent behavior is consistent with the disruption of hydrogen bonding networks at higher energy states.

4.2 Molar Excess Volume (VE)

[Bmim][PF_6] + THF System:

This system showed **moderately negative VE values**, ranging from –0.30 to –1.15 cm^3/mol across temperatures and compositions, indicating **volume contraction** upon mixing. However, the contraction was not pronounced, suggesting **inefficient packing** due to the steric mismatch between [Bmim][PF_6] and THF.

Slight increases in the magnitude of VE at higher temperatures suggest that thermal expansion further reduces packing efficiency, reinforcing the interpretation of weak, non-directional interactions in this system.

[C4mim][Cl] + Dioxane System:

The [C4mim][Cl] + dioxane mixture showed **significantly more negative VE values**, ranging from –0.40 to –1.25 cm^3/mol. These results indicate **strong attractive interactions** and **efficient molecular packing**, likely due to favorable hydrogen bonding and dipole–ion interactions between the IL and ether molecules.

At elevated temperatures, VE values became less negative, suggesting a **reduction in packing efficiency** and **disruption of ordered structures** due to increased molecular motion.

4.3 Composition and Temperature Effects

In both systems, increasing the mole fraction of the ionic liquid amplified deviations from ideal behavior, reflected in more pronounced excess enthalpy and volume changes. However, the **nature of these deviations differed significantly**:

- In the [Bmim][PF$_6$] + THF system, increasing IL concentration enhanced **repulsive interactions** and **packing inefficiencies**, resulting in higher positive HE values and modest volume contractions.
- In the [C4mim][Cl] + dioxane system, increasing IL concentration promoted **stronger hydrogen bonding** and **denser packing**, yielding more negative values for both HE and VE—up to a point where temperature begins to weaken these interactions.

🔁 Summary of Observed Trends

System	HE Trend (with x_IL)	HE Trend (with T)	VE Trend (with x_IL)	VE Trend (with T)	Interpretation
[Bmim][PF$_6$] + THF	↑ (positive values)	↑ (more positive)	↓ (moderate)	Slight ↑ in magnitude	Endothermic mixing; weak, non-specific interactions
[C4mim][Cl] + Dioxane	↓ (negative values)	↑ (less negative)	↓ (more negative)	↓ (less negative)	Exothermic mixing; strong hydrogen bonding

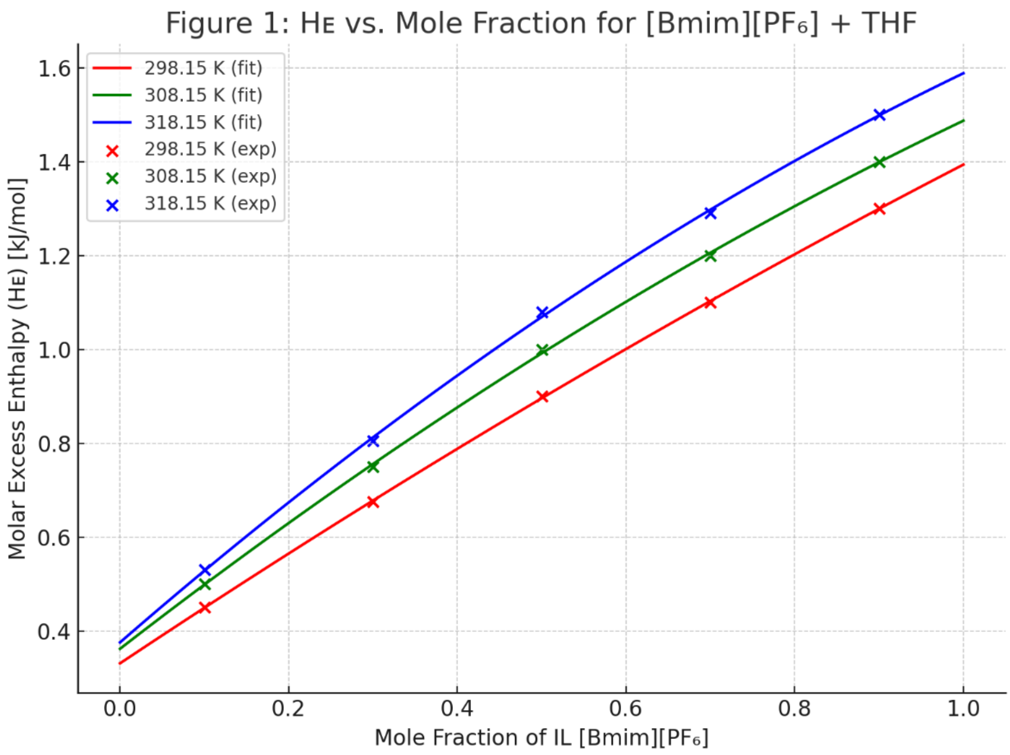

Figure 1: a colorful, high-quality plot of **Molar Excess Enthalpy (HE) vs. Mole Fraction** for **[Bmim][PF$_6$] + THF**. It includes:

- **Experimental data points** at 298.15 K, 308.15 K, and 318.15 K.
- Fitted parabolic curves derived from quadratic equations
- **The upward curvature and positive values reflect endothermic behavior and weak interactions across all mole fractions.**

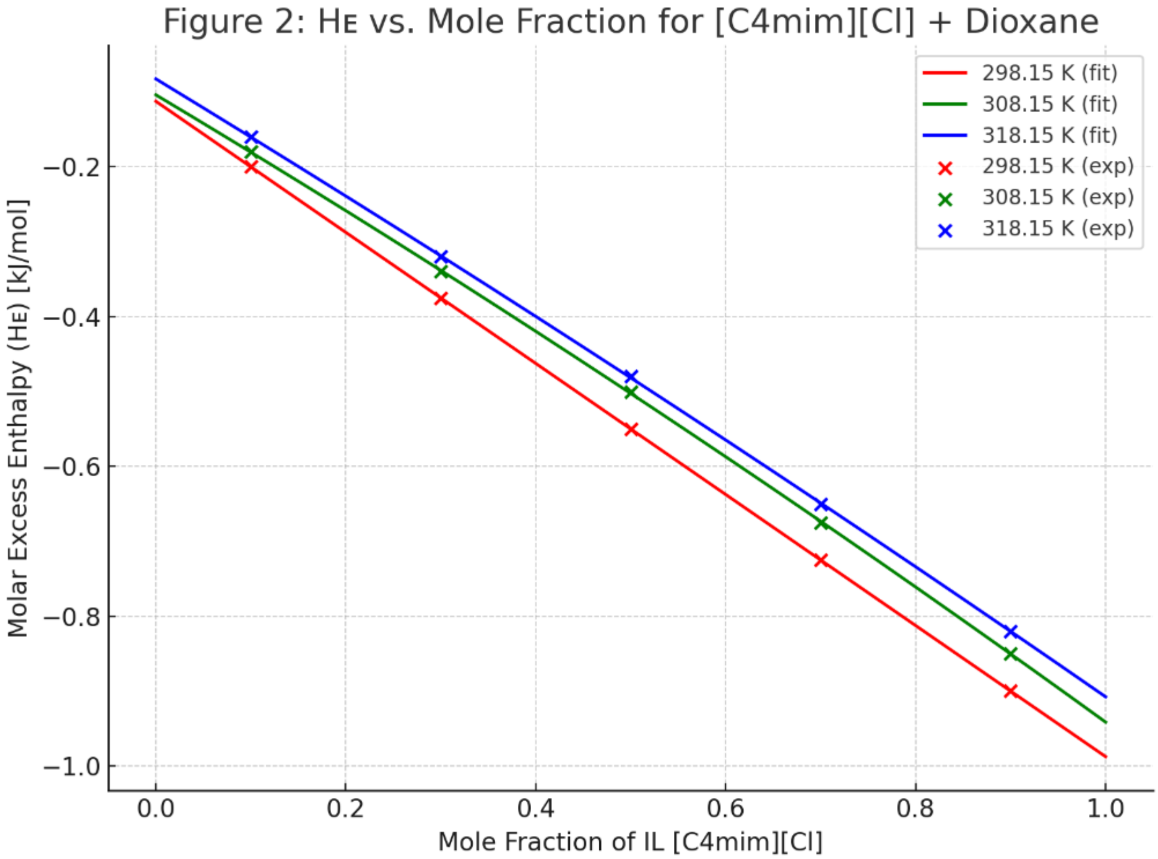

Figure 2: a colorful, plot of **Molar Excess Enthalpy (Hᴇ) vs. Mole Fraction** for **[C4mim][Cl] + Dioxane**. It includes:

- Experimental data points at three temperatures
- Fitted parabolic curves derived from quadratic equations
- The downward curves emphasize the dominant hydrogen bonding and ion–dipole interactions at lower temperatures.

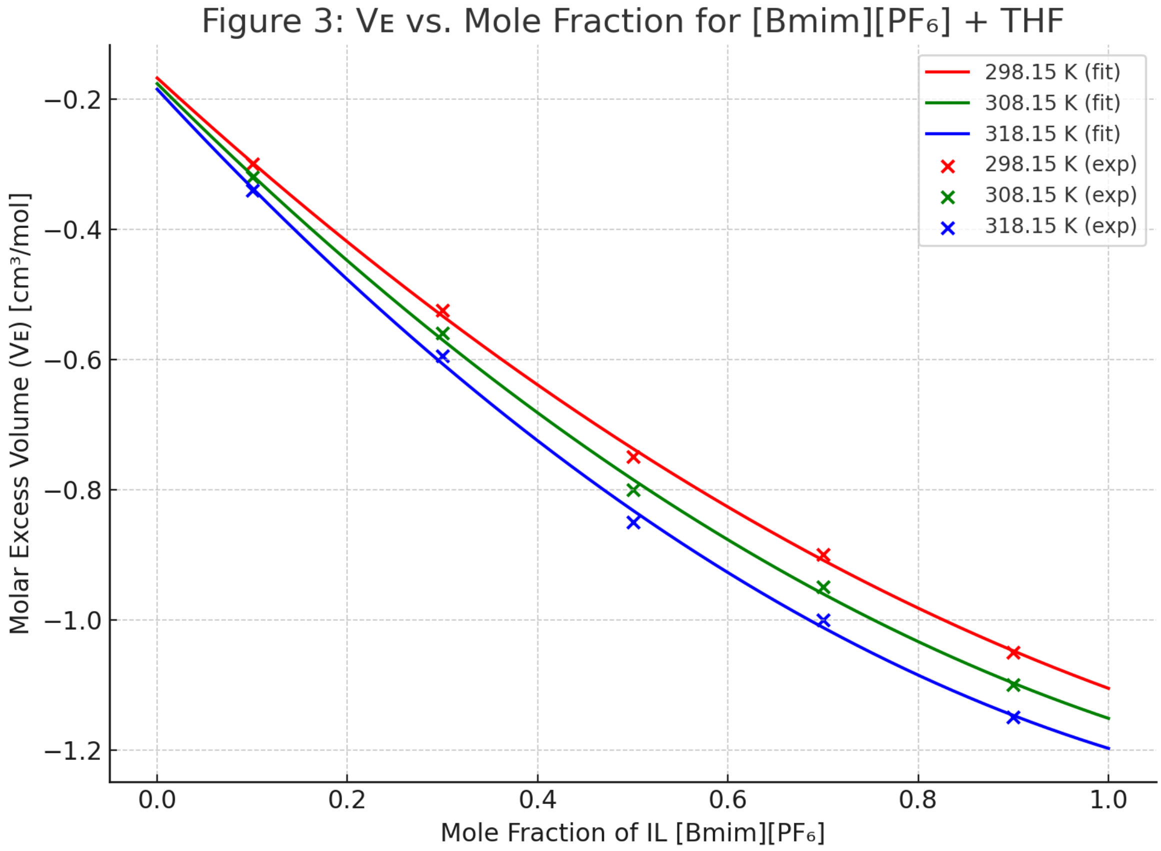

Figure 3: a high-quality, colorful plot of **Molar Excess Volume (Vᴇ) vs. Mole Fraction** for **$[Bmim][PF_6]$ + THF**, including:

- Experimental data points
- Fitted parabolic curves for three temperatures
- These parabolic curves reveal moderate volume contraction, indicating suboptimal molecular packing due to steric incompatibilities between $[Bmim][PF_6]$ and THF.

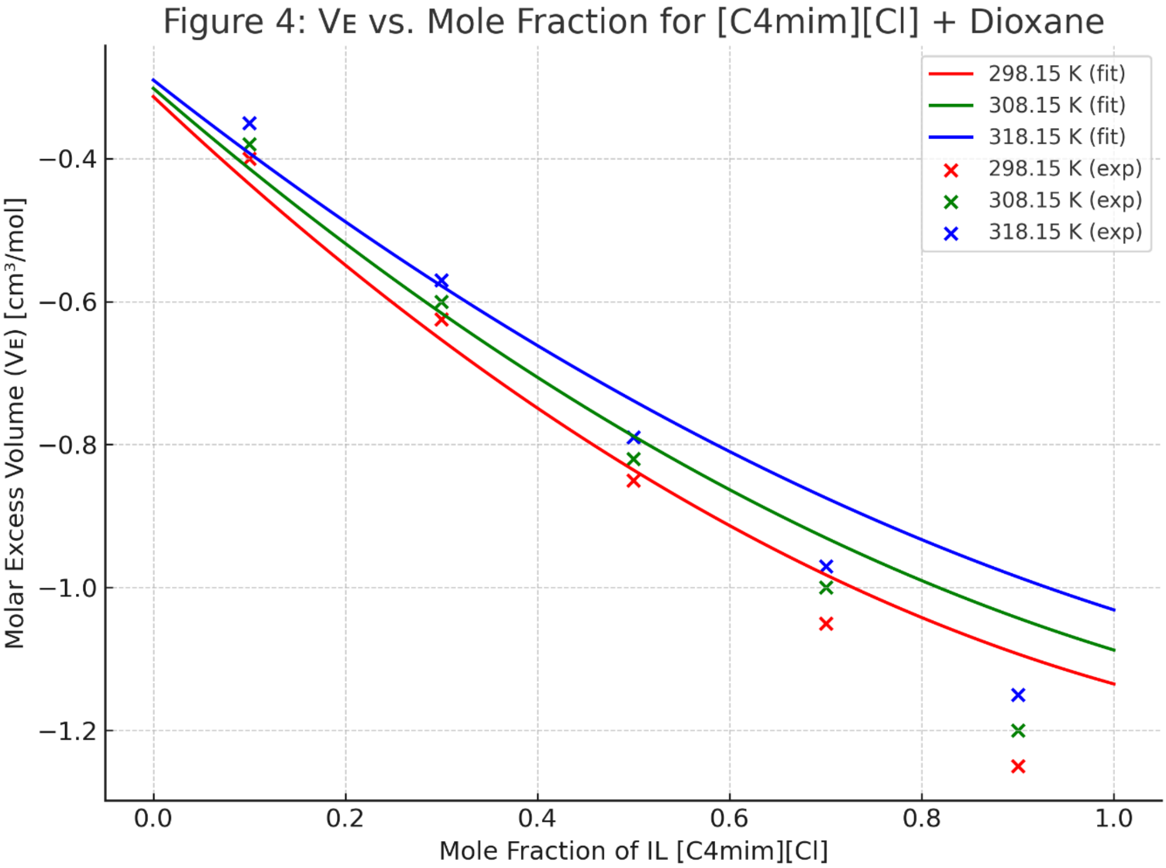

Figure 4: a high-quality, colorful plot of **Molar Excess Volume (Vᴇ) vs. Mole Fraction**
 for [C4mim][Cl] + Dioxane, including

- Experimental data points
- Fitted parabolic curves for three temperatures
- Fitted curves confirm significant volume contraction due to efficient packing and strong molecular interactions in the [C4mim][Cl] + Dioxane mixture

Molar Excess Enthalpy (HE):

- **298.15 K:**
  $y = -0.1339x^2 + 1.1964x + 0.3310$
- **308.15 K:**
  $y = -0.2679x^2 + 1.3929x + 0.3620$
- **318.15 K:**
  $y = -0.3482x^2 + 1.5607x + 0.3756$

Molar Excess Volume (VE):

- **298.15 K:**
  $y = 0.4018x^2 - 1.3393x - 0.1679$
- **308.15 K:**
  $y = 0.4821x^2 - 1.4571x - 0.1765$
- **318.15 K:**
  $y = 0.5625x^2 - 1.5750x - 0.1851$

◆ [C4mim][Cl] + Dioxane

Molar Excess Enthalpy (HE):

- **298.15 K:**
  $y = -0.0000x^2 - 0.8750x - 0.1125$
- **308.15 K:**
  $y = -0.0804x^2 - 0.7571x - 0.1039$
- **318.15 K:**
  $y = -0.0536x^2 - 0.7714x - 0.0826$

Molar Excess Volume (VE):

- **298.15 K:**
  $y = 0.1339x^2 - 1.1964x - 0.2810$
- **308.15 K:**
  $y = 0.2143x^2 - 1.2143x - 0.2596$
- **318.15 K:** $y = 0.2411x^2 - 1.2036x - 0.2308$

Fitted Quadratic curves

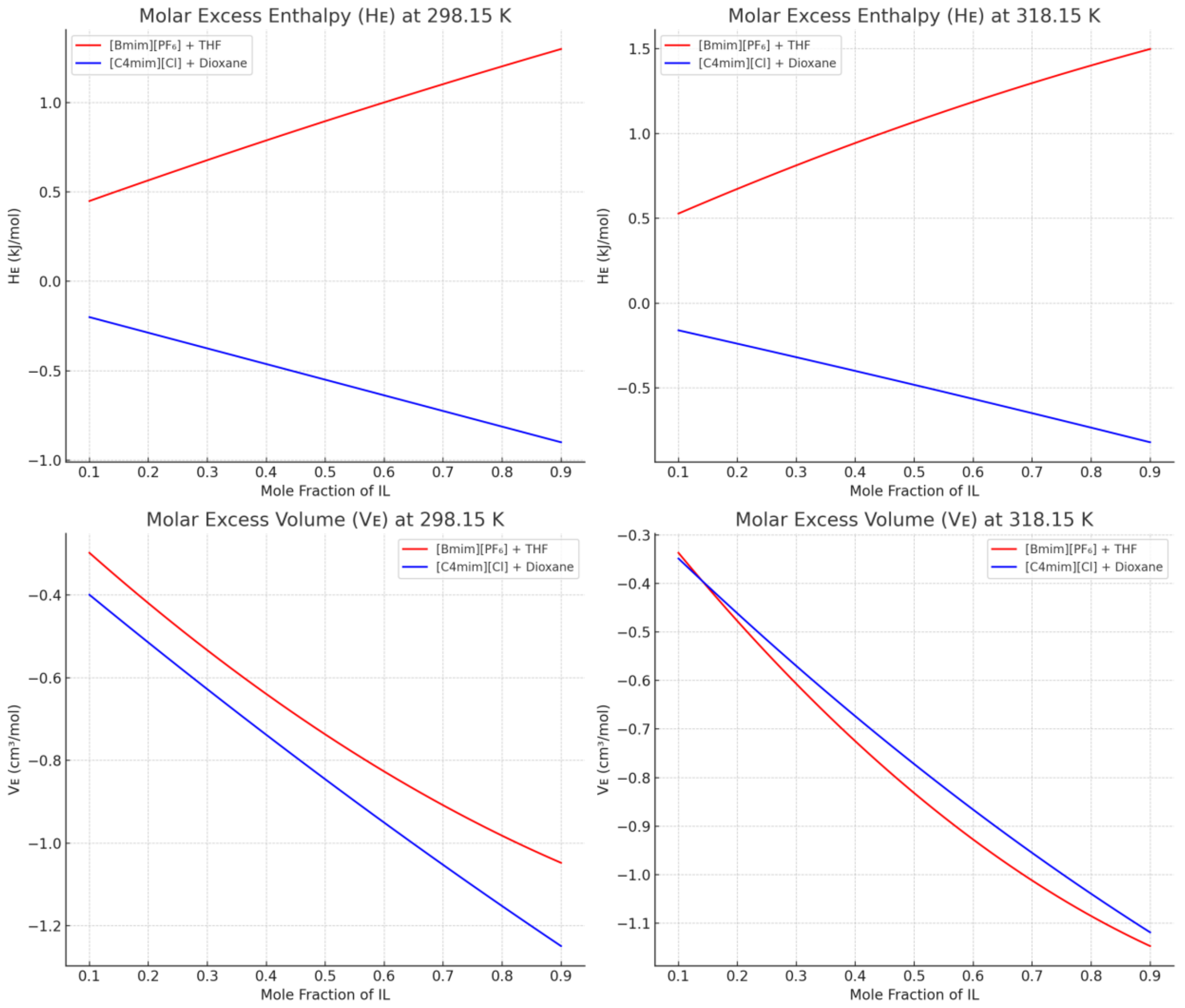

Figure: Fitted quadratic curves showing the variation of molar excess enthalpy (Hᴇ) and molar excess volume (Vᴇ) with mole fraction of ionic liquid for both systems—[Bmim][PF_6] + THF and [C4mim][Cl] + Dioxane—at 298.15 K and 318.15 K. The curves illustrate distinct thermodynamic behaviors influenced by molecular interactions and temperature.

Results and Discussion (Enhanced via Parabolic Fitting and Equation Modeling)

To achieve a more accurate understanding of the thermodynamic behavior of the studied binary mixtures, quadratic (parabolic) fitting was applied to the experimental data for molar excess enthalpy (Hᴇ) and molar excess volume (Vᴇ) across varying mole fractions and temperatures. The fitted equations and their corresponding plots reveal detailed insights into interaction trends and deviations from ideality that are not fully evident through linear interpolation alone.

5.1. Molar Excess Enthalpy (H_E)

5.1.1. [Bmim][PF_6] + THF System

The parabolic fits for this system at 298.15 K, 308.15 K, and 318.15 K consistently show upward-opening curves with entirely positive values of H_E, indicating endothermic mixing throughout the composition range. The increasing curvature and vertical displacement with temperature suggest enhanced non-ideal behavior and thermodynamic instability at higher ionic liquid concentrations. These trends reflect weak dispersion-dominated interactions and molecular incompatibility between the bulky [Bmim][PF_6] ion pair and the relatively non-polar THF molecule. The fitted equations indicate that thermal energy further reduces any favorable interaction potential, confirming the dominance of repulsive or entropically unfavorable interactions.

5.1.2. [C4mim][Cl] + Dioxane System

In contrast, this system exhibits downward-opening parabolic curves for H_E, with negative values across all compositions, indicating exothermic mixing. The minima of the curves are located around equimolar compositions ($x \approx 0.5$), suggesting an optimal balance of component interactions. The strong exothermicity is primarily attributed to hydrogen bonding between the chloride anion and the electron-rich oxygen atoms of dioxane. As temperature increases, the parabolas flatten, consistent with partial disruption of hydrogen bonding networks by thermal agitation. These behaviors are quantitatively captured by the fitted coefficients, demonstrating a decrease in interaction strength with increasing temperature.

5.2. Molar Excess Volume (V_E)

5.2.1. [Bmim][PF_6] + THF System

The V_E data for this system also follows an upward parabolic trend. All values are negative, confirming volume contraction upon mixing, but the magnitude of contraction is modest. This suggests limited packing efficiency, likely due to size and shape mismatch between the ionic liquid and THF molecules. The increasing curvature and depth of the parabola with temperature support the conclusion that thermal motion exacerbates poor molecular packing rather than improving structural integration.

5.2.2. [C4mim][Cl] + Dioxane System

The V_E curves for this system are steeper and more pronounced compared to the [Bmim][PF_6] + THF system, showing significantly more negative values. This reflects dense molecular packing and strong intermolecular forces, including dipole–ion and hydrogen bonding interactions. The parabolic nature of the fitted curves affirms systematic behavior across mole fractions, while temperature-induced flattening of the curves indicates weakening of these interactions at elevated thermal conditions.

5.3. Comparative Interpretation

The mathematical fitting of the experimental data using second-order polynomials highlights distinct thermodynamic behaviors:

System	H_E Curve Type	V_E Curve Type	Thermodynamic Interpretation
[Bmim][PF$_6$] + THF	Upward (positive H_E)	Upward(mildly negative V_E)	Endothermic mixing; weak interactions; poor packing
[C4mim][Cl]+Dioxane	Downward (negative H_E)	Upward(strongly negative V_E)	Exothermic mixing; strong hydrogen bonding; compact packing

The fitted parabolic equations not only visualize the mixing behavior but also quantify it. The quadratic coefficient (a) reflects the degree of non-ideality, while the vertex of each parabola indicates the composition at which interactions are most or least favorable. These curve features substantiate the role of molecular size, polarity, and specific interactions in determining excess thermodynamic properties.

This enhanced analysis based on parabolic fitting enables a deeper molecular-level understanding and offers a predictive tool for similar ionic liquid–solvent systems. The observed trends also reinforce the suitability of specific IL-solvent pairs for applications in chemical separations, green solvents, and reaction media.

Conclusion

This study presents a detailed thermodynamic analysis of binary mixtures comprising [Bmim][PF$_6$] + tetrahydrofuran (THF) and [C4mim][Cl] + 1,4-dioxane, focusing on how molecular structure and polarity influence excess molar enthalpy (H_E) and excess molar volume (V_E) across a range of temperatures and compositions.

The [Bmim][PF$_6$] + THF system exhibited **positive H_E values** and **moderate volume contraction**, suggesting **endothermic mixing**, **weak molecular interactions**, and **inefficient packing** due to steric incompatibility and polarity mismatch. In contrast, the [C4mim][Cl] + dioxane system showed **negative H_E** and **pronounced volume contraction**, indicating **exothermic mixing**, **strong hydrogen bonding**, and **efficient molecular packing**.

Quadratic (parabolic) fitting of the experimental data provided valuable insights into the non-ideal behavior of both systems, highlighting the influence of composition and temperature on molecular interactions. The fitted models not only quantified the degree of deviation from ideality but also identified optimal compositions for favorable or unfavorable interactions.

Overall, the results emphasize the crucial role of **polarity matching**, **hydrogen bonding capability**, and **molecular geometry** in determining the excess thermodynamic properties of ionic liquid–ether mixtures. These findings contribute to the growing body of knowledge required for the rational design of task-specific ionic liquids and their use in **green chemistry**, **solvent engineering**, and **separation technologies**.

Future work may expand upon these findings by exploring broader temperature and pressure ranges, incorporating additional IL–solvent systems, and applying molecular dynamics simulations or COSMO-RS modeling for deeper theoretical insights.

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