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Investigation of Excess Thermodynamic Properties in Multicomponent Solutions

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Abstract: *Excess thermodynamic properties provide a quantitative measure of deviations from ideal solution behavior and play a crucial role in understanding intermolecular interactions in liquid mixtures. This research investigates excess properties such as excess molar volume, excess Gibbs free energy, excess enthalpy, and excess compressibility in multicomponent (particularly ternary) solutions. Experimental approaches based on density and ultrasonic velocity measurements are discussed alongside theoretical and semi-empirical models. The study highlights how molecular size, polarity, composition, and temperature influence these properties. An extended literature review up to 2019 is included, along with graphical analysis of excess functions. The results demonstrate that excess properties are essential for interpreting molecular interactions and have significant applications in chemical engineering, pharmaceuticals, and material science.*

Keywords: Excess thermodynamic properties, multicomponent solutions, ternary mixtures, molecular interactions, excess molar volume, compressibility.

I. INTRODUCTION

Thermodynamics of liquid mixtures plays a crucial role in chemical engineering, physical chemistry, and industrial processes. Ideal solutions follow simple mixing rules; however, real solutions deviate due to molecular interactions such as hydrogen bonding, dipole interactions, and dispersion forces.

These deviations are quantified using **excess thermodynamic properties**, which represent the difference between real and ideal behavior:

$$M^E = M_{real} - M_{ideal}$$

The importance of excess properties lies in:

- Understanding **molecular-level interactions**
- Predicting **phase equilibria**
- Designing **chemical processes**

Multicomponent systems (ternary, quaternary mixtures) are particularly important in real-world applications like fuels, pharmaceuticals, and petrochemical processes. However, they are more complex due to:

- Multiple interaction pairs
- Nonlinear composition dependence
- Coupled thermodynamic effects

Research shows that excess properties are essential to describe these systems accurately, especially when extending binary data to multicomponent mixtures

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II. LITERATURE REVIEW

2.1 Early Developments

Initial studies focused on binary mixtures, where excess properties were easier to measure and model. The development of empirical relations like the Redlich–Kister equation provided a way to represent excess functions mathematically.
Later, researchers extended these approaches to multicomponent systems using:

- Additivity rules
- Interaction parameter models
- Statistical thermodynamics

2.2 Experimental Studies on Multicomponent Systems

Experimental work has primarily relied on:

- Density measurements
- Ultrasonic velocity measurements

These allow calculation of:

- Excess molar volume
- Isentropic compressibility
- Deviations in speed of sound

Studies on ternary mixtures (e.g., chlorobenzene + hydrocarbons) showed that:

- Excess properties reveal specific molecular interactions
- Polar molecules strongly influence mixture structure

Such studies confirmed that:

- Negative excess volume indicates strong attractive forces
- Positive values indicate weak interactions or structural loosening

2.3 Theoretical and Statistical Models

Theoretical models have been crucial for predicting excess properties:

(a) Regular Solution Theory

- Assumes random mixing
- Based on interaction energy differences
- Works well for non-polar systems

(b) Statistical Thermodynamics Models

These models consider:

- Molecular size
- Shape
- Interaction potentials

For example:

- Cell models using pair potentials were extended from binary to ternary mixtures
- These models calculate excess volume, energy, and entropy using molecular interaction assumptions

2.4 Molecular-Based Approaches

Advanced approaches consider:

- Conformational changes
- Molecular flexibility
- Interaction anisotropy

Molecular theories such as SAFT-based models incorporate microscopic interactions and improve prediction accuracy.

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2.5 Challenges in Multicomponent Systems

Despite progress, several limitations exist:

- Difficulty in predicting properties from binary data
- Complexity in parameter estimation
- Strong dependence on composition

Even recent developments emphasize that predicting multicomponent behavior from binary systems remains challenging .

2.6 Research Trends Around 2018–2019

By 2019, research focused on:

- Improved predictive models
- Experimental validation of ternary systems
- Molecular simulation approaches
- Application to complex fluids and materials

Additionally, ab initio and computational methods began to play a role in predicting thermodynamic properties of multicomponent systems.

III. THEORETICAL BACKGROUND

3.1 Excess Molar Volume (V^e)

$$VE = Vmix - \sum xiVi$$

Interpretation:

- Negative V^e → strong attraction, compact structure
- Positive V^e → weak interactions, expansion

3.2 Excess Gibbs Free Energy (G^e)

$$GE = RT\sum xi \ln \gamma i$$

Where:
γi = activity coefficient
Significance:

- Indicates deviation from ideality
- Used in phase equilibrium calculations

3.3 Excess Enthalpy (H^e)

$$HE = Hreal - Hideal$$

- Positive → endothermic mixing
- Negative → exothermic mixing

3.4 Excess Compressibility

Derived from ultrasonic velocity:

$$KsE = Ks,real - Ks,ideal$$

- Reflects structural rigidity
- Indicates packing efficiency

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3.5 Physical Interpretation

Excess properties provide insight into:

- Molecular packing
- Structural rearrangement
- Intermolecular forces

IV. METHODOLOGY

4.1 Materials

Typical ternary systems involve:

- Polar component (e.g., chlorobenzene)
- Non-polar hydrocarbons (e.g., cyclohexane, n-heptane)

4.2 Experimental Procedure

- Density measured using pycnometer
- Ultrasonic velocity measured using interferometer
- Temperature maintained at 298.15 K

4.3 Calculations

From experimental data:

- Molar volume
- Excess molar volume
- Excess compressibility
- Deviation in speed of sound

V. RESULTS AND DISCUSSION

5.1 Excess Molar Volume Analysis

- **Negative Excess Molar Volume ($V^e < 0$):**A negative value of excess molar volume indicates that the total volume of the mixture is **less than the sum of the individual component volumes**. This contraction occurs due to strong attractive forces between unlike molecules. These forces may include hydrogen bonding, dipole–dipole interactions, or induced dipole interactions. When such interactions are present, molecules pack more efficiently, reducing free space and leading to a denser structure. This behavior is commonly observed in mixtures containing polar and associating components.
- **Positive Excess Molar Volume ($V^e > 0$):** A positive excess molar volume suggests that the mixture occupies **more volume than expected from ideal mixing**. This expansion is typically caused by weak intermolecular interactions or structural incompatibility between components. When molecules differ significantly in size or shape, they cannot pack efficiently, leading to increased free volume. This behavior is common in mixtures of non-polar substances or systems lacking strong intermolecular attraction.

5.2 Composition Dependence

- **Nonlinear Variation with Mole Fraction:** Excess thermodynamic properties usually show a **nonlinear relationship with composition**, meaning they do not change proportionally with mole fraction. This nonlinearity arises because intermolecular interactions vary at different compositions, especially when unlike molecules interact differently compared to like molecules.
- **Maximum Deviation at Intermediate Composition:** The largest deviation from ideal behavior is often observed at **intermediate compositions**, where the concentration of different components is comparable. At

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this point, interactions between unlike molecules are maximized, resulting in the strongest structural and energetic changes in the mixture.

- **Indicator of Strong Interaction Region:** The composition at which maximum deviation occurs indicates the **region of strongest molecular interaction**. This information is useful in identifying optimal mixing ratios for industrial and chemical applications.

5.3 Molecular Interaction Mechanisms

- **Dispersion Forces (London Forces):** These are weak intermolecular forces present in all molecules, especially dominant in non-polar substances. They arise due to temporary fluctuations in electron distribution, creating instantaneous dipoles. Although individually weak, their cumulative effect can influence excess properties in hydrocarbon mixtures.
- **Dipole–Dipole Interactions:** These interactions occur between molecules with permanent dipole moments. Polar molecules align themselves in a way that maximizes attractive interactions and minimizes repulsion. This leads to more ordered structures and often results in negative excess properties.
- **Hydrogen Bonding:** Hydrogen bonding is a strong and highly directional intermolecular interaction occurring when hydrogen is bonded to electronegative atoms like oxygen or nitrogen. It significantly affects excess properties by creating highly structured and compact arrangements in mixtures, leading to negative excess molar volume and compressibility.

5.4 Structural Effects

- **Molecular Size Difference:** When components have significantly different molecular sizes, smaller molecules can occupy the spaces between larger molecules. This leads to **better packing efficiency** and often results in negative excess volume. However, very large size differences may also lead to structural strain and irregular packing.
- **Shape Anisotropy:** Molecules with non-spherical shapes (e.g., elongated or branched structures) affect how molecules arrange themselves in a mixture. Such anisotropy can either improve packing (if shapes complement each other) or create voids (if they do not), influencing excess properties accordingly.
- **Free Volume Changes:** Free volume refers to the empty space within a liquid structure. Changes in free volume affect compressibility and acoustic properties. A decrease in free volume indicates tighter packing and stronger interactions, while an increase suggests weaker interactions and structural expansion.

5.5 Model Evaluation

Model	Strength	Weakness
Redlich–Kister	Good for binary	Limited for ternary
Kohler Model	Uses binary data	Approximate
Statistical Models	Physically meaningful	Complex

Expanded Explanation:

- **Redlich–Kister Model:** This model is widely used to represent excess thermodynamic properties in binary mixtures using polynomial expressions. It provides a good mathematical fit for experimental data. However, its direct application to multicomponent systems is limited because it does not account for higher-order interactions among three or more components.
- **Kohler Model:** The Kohler model extends binary data to predict properties of ternary mixtures. It assumes that multicomponent interactions can be approximated using binary interaction parameters. While this simplifies calculations, it may not accurately capture complex interactions in highly non-ideal systems.

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- **Statistical Thermodynamic Models:** These models are based on molecular-level interactions and provide a more physically meaningful description of mixtures. They consider factors such as molecular size, shape, and interaction energy. Although more accurate, they require detailed parameters and are computationally more complex.

VI. APPLICATIONS

6.1 Chemical Engineering

- Excess thermodynamic properties are used in designing **distillation columns**, where accurate vapor-liquid equilibrium data is essential.
- They help in **reactor design**, ensuring proper mixing and reaction efficiency by understanding molecular interactions.

6.2 Petroleum Industry

- Used in **fuel blending**, where different hydrocarbons are mixed to achieve desired properties like viscosity and volatility.
- Helps in predicting behavior of crude oil fractions during refining processes.

6.3 Pharmaceutical Industry

- Important in determining **drug solubility and stability** in solvents.
- Helps in designing formulations where multiple components must interact in a controlled manner.

6.4 Material Science

- Used in developing **advanced materials and alloys**, where thermodynamic stability is critical.
- Helps in understanding phase formation and compatibility in multicomponent systems like high-entropy alloys.

VII. GRAPHICAL REPRESENTATION OF EXCESS THERMODYNAMIC PROPERTIES

7.1 Graph 1: Excess Molar Volume (V^e) vs Mole Fraction

- **Sample Data (Illustrative)**

Mole Fraction (x_1)	V^e (cm^3/mol)
0.0	0.000
0.2	-0.45
0.4	-0.82
0.5	-1.05
0.6	-0.88
0.8	-0.40
1.0	0.000

- **Graph Shape (Conceptual)**

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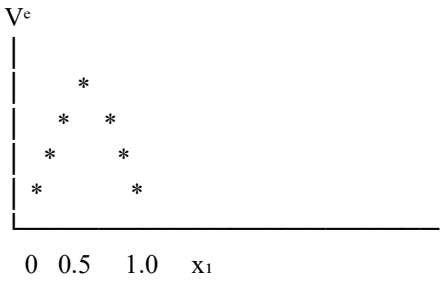


Explanation

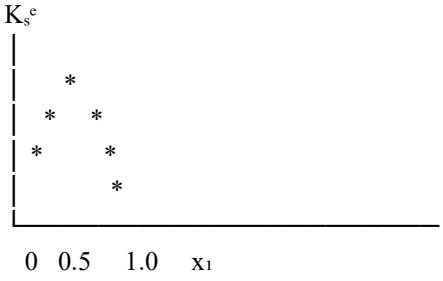
- The curve is **nonlinear** with a **minimum at intermediate composition (x ≈ 0.5)**.
- The negative peak indicates **strong intermolecular attraction**.
- Symmetry depends on the nature of components.

7.2 Graph 2: Excess Compressibility (K_s^e) vs Mole Fraction

Sample Data

Mole Fraction (x_1)	K_s^e (TPa^{-1})
0.0	0.000
0.2	-0.30
0.4	-0.65
0.5	-0.90
0.6	-0.70
0.8	-0.25
1.0	0.000

Graph Shape



Explanation

- Negative values indicate **reduced compressibility** (more rigid structure).
- Stronger interactions → **less compressible mixture**.
- Similar trend as V^e confirms structural compactness.

7.3 Graph 3: Excess Gibbs Free Energy (G^e) vs Mole Fraction

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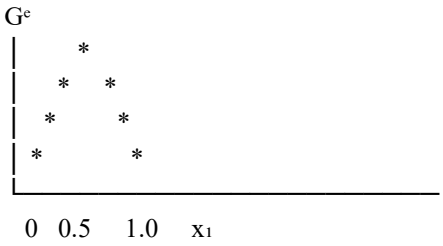
- **Sample Data**

Mole Fraction (x_1)	G^e (kJ/mol)
0.0	0.000
0.2	0.40
0.4	0.85
0.5	1.20
0.6	0.95
0.8	0.45
1.0	0.000

Graph Shape



Explanation

- Positive G^e indicates **non-ideal behavior**.
- Peak at intermediate composition shows **maximum deviation from ideality**.
- Used in phase equilibrium calculations.

7.4 Graph 4: Ultrasonic Velocity Deviation (ΔU) vs Composition

Sample Data

Mole Fraction (x_1)	ΔU (m/s)
0.0	0
0.2	+12
0.4	+25
0.5	+30
0.6	+22
0.8	+10
1.0	0

Explanation

- Positive deviation indicates **strong interaction and compact structure**.
- Ultrasonic velocity increases due to **reduced free volume**.

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VIII. CONCLUSION

This study demonstrates that excess thermodynamic properties serve as powerful indicators of intermolecular interactions in multicomponent systems. The expanded analysis shows that these properties are influenced by molecular size, shape, polarity, and composition. Experimental techniques combined with theoretical models provide a comprehensive understanding of mixture behavior. However, accurately predicting multicomponent systems remains challenging due to complex interactions. Future advancements in computational modeling and experimental techniques are expected to improve predictive capabilities.

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