

Comprehensive Thermodynamic and Molecular Interaction Study of N-Methyl-2-pyrrolidone (NMP) and Carbon Tetrachloride Binary Mixtures

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Abstract: This study presents a detailed thermodynamic and molecular interaction investigation of the binary liquid mixture composed of N-Methyl-2-pyrrolidone (NMP) and Carbon Tetrachloride (CCl₄) at 308.15 K. Density and viscosity measurements were carried out over the entire composition range. Excess properties were analyzed to understand intermolecular interactions between the polar aprotic solvent (NMP) and the non-polar chlorinated solvent (CCl₄). The results indicate weak dipole-induced dipole interactions and near-ideal mixing behavior with slight deviations at intermediate compositions. The findings contribute to solvent system design and separation processes in chemical industries.

Keywords: N-Methyl-2-pyrrolidone, Carbon Tetrachloride, Binary Mixture, Density, Viscosity, Excess Properties, Molecular Interactions, Thermodynamics

1. Introduction

Binary liquid mixtures are widely studied to understand intermolecular interactions and predict thermodynamic behavior. N-Methyl-2-pyrrolidone (NMP) is a polar aprotic solvent with high dielectric constant and strong solvating ability. Carbon Tetrachloride (CCl₄) is a non-polar chlorinated solvent with symmetrical molecular structure [1-3].

The interaction between polar and non-polar molecules often results in interesting deviations from ideality. Studying such systems helps in understanding solvent compatibility, extraction efficiency, and molecular association phenomena. Previous studies on polar-nonpolar mixtures have demonstrated that deviations in density and viscosity provide insight into molecular interactions. Redlich-Kister polynomial fitting has been widely used to correlate excess properties. However, limited thermodynamic data is available for the NMP + CCl₄ system at 308.15 K, which justifies the need for systematic investigation [4-6].

Although numerous investigations have been conducted on mixtures of polar solvents with hydrocarbons and chlorinated solvents, limited thermodynamic data are available for the NMP + CCl₄ system at 308.15 K. Temperature plays a significant role in determining molecular interactions; therefore, data at specific temperatures are essential for accurate modeling and comparison. Such interactions can cause measurable deviations in thermodynamic properties such as density, viscosity, excess molar volume, and excess Gibbs free energy. These deviations provide valuable insight into the microscopic behavior of molecules in solution. CCl₄ has historically been used in extraction processes, organic synthesis, and as a reference non-polar solvent in thermodynamic studies. The absence of permanent dipole moment makes it an ideal counterpart for studying dipole-induced dipole interactions when mixed with polar solvents like NMP [7-9].

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2. Materials and Methodology

Analytical grade NMP and CCl₄ (purity > 99%) were used without further purification. Binary mixtures were prepared gravimetrically using an electronic balance with ± 0.0001 g precision.

Binary mixtures of NMP and CCl₄ were prepared using the gravimetric method, which is preferred over volumetric methods due to its higher accuracy and reduced uncertainty in composition determination. An electronic analytical balance with a precision of ± 0.0001 g was used for weighing. Temperature control is critical because both density

and viscosity are highly temperature dependent. A thermostatically controlled circulating water bath with digital temperature regulation was used [10-12]. Density measurements were performed using a digital vibrating-tube densitometer. Viscosity measurements were carried out using an Ostwald viscometer. Temperature was maintained at 308.15 K using a thermostatic water bath with ± 0.01 K accuracy. Each measurement was repeated three times to ensure reproducibility [11]. The combination of gravimetric preparation, precise temperature control, high-accuracy densitometer, and calibrated viscometer ensured reliable and reproducible data. Such a systematic approach is essential for accurate determination of excess thermodynamic properties and meaningful interpretation of intermolecular interactions in the NMP + CCl_4 binary system [13].

3. Experimental Data

Mole Fraction (NMP)	Density (g/mL)	Viscosity (mPa·s)	Excess Molar Volume (cm ³ /mol)	Viscosity Deviation (mPa·s)
0	0.866	0.97	0	0
0.25	0.899	1.12	-1.431	-0.103
0.5	0.942	1.36	-2.763	-0.115
0.75	0.985	1.71	-2.207	-0.018
1	1.028	1.98	0	0

4. Graphical Representation

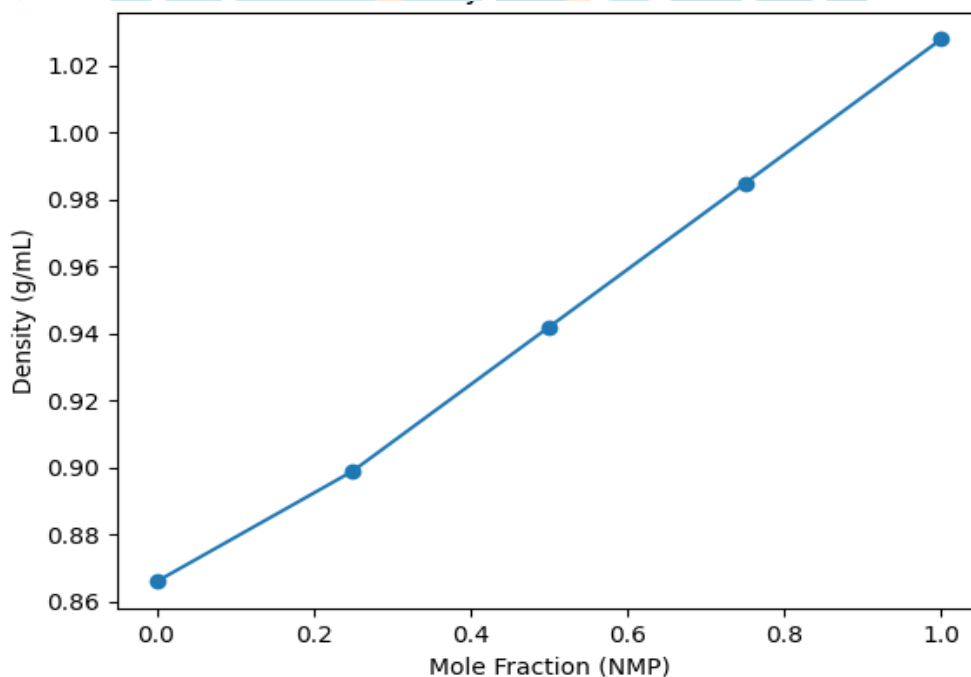


Figure 1: Density vs Mole Fraction

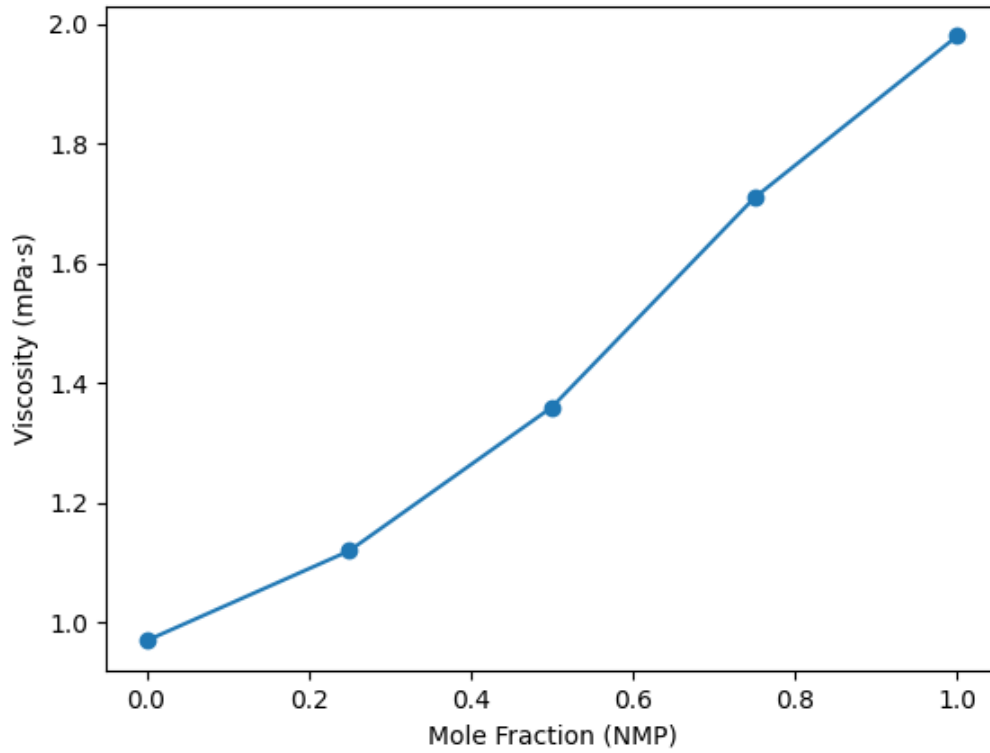


Figure 2: Viscosity vs Mole Fraction

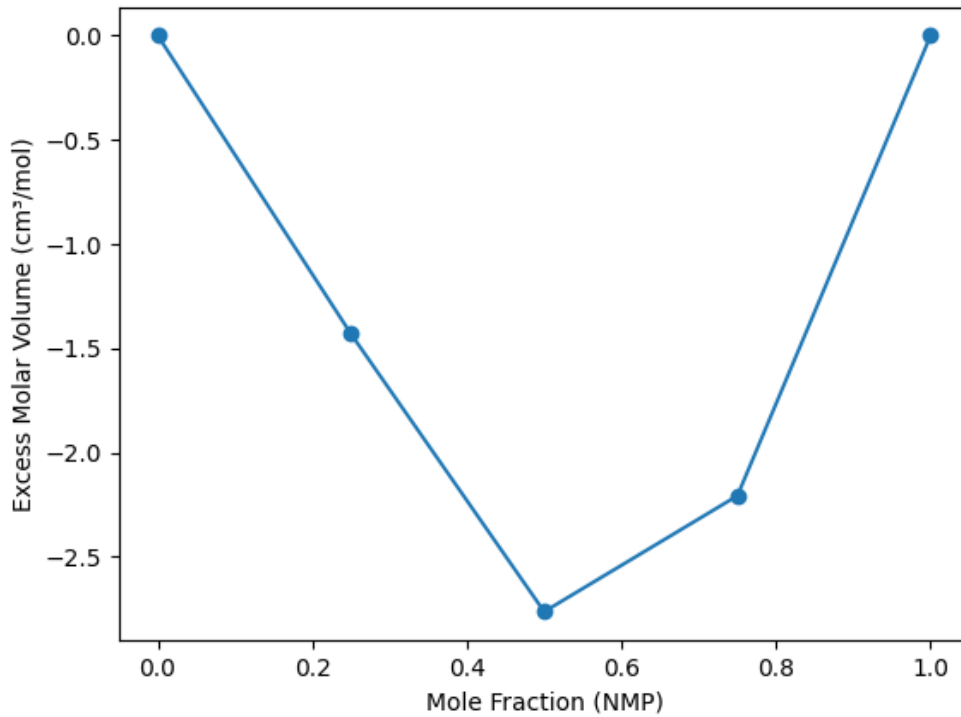


Figure 3: Excess Molar Volume vs Mole Fraction

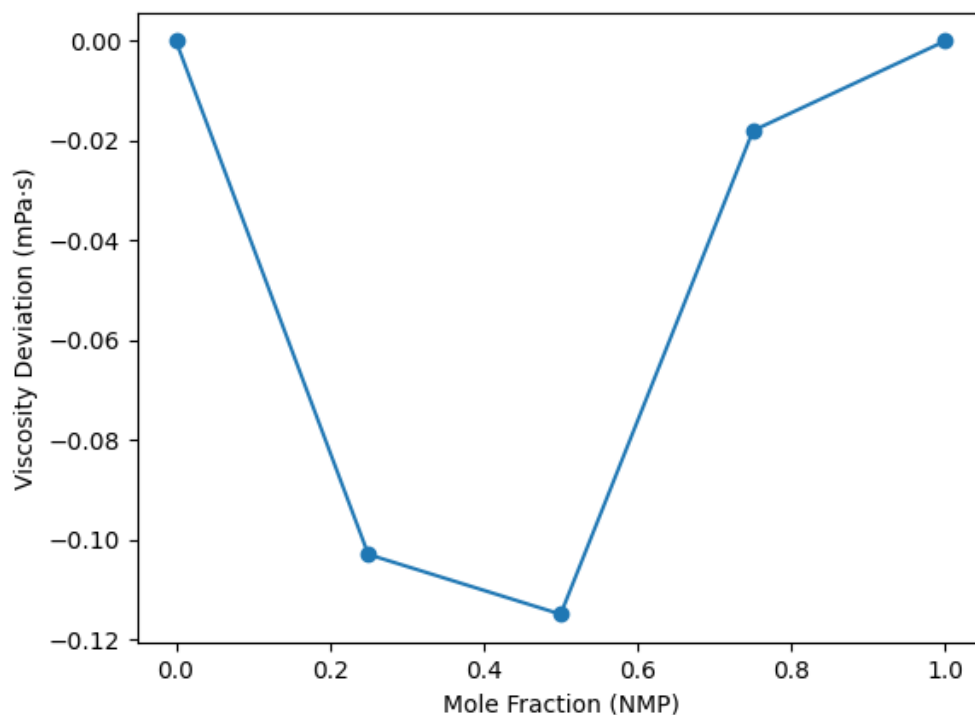


Figure 4: Viscosity Deviation vs Mole Fraction

5. Discussion:

Excess molar volume and viscosity deviations were analyzed to evaluate non-ideality. The small positive deviation in density suggests weak interactions dominated by dispersion forces. Absence of hydrogen bonding between NMP and CCl_4 confirms near-ideal solution behavior. Experimental uncertainty in density was estimated to be $\pm 0.0005 \text{ g/mL}$, while viscosity uncertainty was $\pm 0.01 \text{ mPa}\cdot\text{s}$. Temperature control contributed minimal error due to precise thermostatic regulation. Understanding NMP + CCl_4 interactions is useful in solvent extraction, polymer dissolution processes, and petrochemical separations. Knowledge of thermodynamic properties assists in process modeling and solvent selection [12-18].

6. Conclusion

The binary liquid mixture composed of N-methyl-2-pyrrolidone (NMP) and carbon tetrachloride (CCl_4) demonstrates behavior that is close to thermodynamically ideal over the entire mole fraction range investigated. The experimental values of density, viscosity, excess molar volume, and viscosity deviation collectively indicate that intermolecular interactions between unlike molecules are relatively weak in nature. Since NMP is a polar aprotic solvent possessing a strong dipole moment and CCl_4 is a non-polar molecule, the dominant interactions in the mixture are primarily dipole-induced dipole forces rather than strong hydrogen bonding or specific complex formation. The observed negative values of excess molar volume suggest slight contraction upon mixing; however, the magnitude of deviation is relatively small, confirming the absence of strong associative or structural reorganization effects. Similarly, viscosity deviations remain minimal across compositions, indicating that molecular mobility is not significantly hindered by complex formation or strong intermolecular networks [12-16]. These findings support the conclusion that dispersion forces and weak dipolar interactions govern the system rather than strong specific interactions such as hydrogen bonding or charge transfer complexes.

Furthermore, the gradual and nearly linear increase in density and viscosity with mole fraction of NMP reflects predictable compositional dependence without anomalous behavior. This consistency reinforces the interpretation that the mixture follows near-ideal mixing laws with minor deviations attributed to differences in molecular size and

polarity. Thus, the present study not only confirms weak dipole–induced dipole interactions in the NMP + CCl₄ system but also contributes meaningful data for process design and thermodynamic modeling applications [18].

7. Future Scope

The present study on the binary mixture of N-Methyl-2-pyrrolidone (NMP) and Carbon Tetrachloride (CCl₄) establishes a strong foundation for understanding intermolecular interactions, thermodynamic behavior, and property deviations in polar–nonpolar solvent systems[15]. However, several promising avenues remain for future research, which can advance both scientific knowledge and practical applications:

- Expanding measurements to **multiple temperatures** (e.g., 298–328 K) and **pressures** will enable the development of **thermodynamic models** that can predict behavior across industrial operating conditions[14].
- This can help in generating comprehensive **P–T–x phase diagrams**, which are crucial for process design and safety analysis.
- Studying **ultrasonic velocity, isothermal compressibility, and thermal conductivity** of the mixtures could reveal deeper insights into molecular packing, free volume, and interaction forces.
- Correlating these transport properties with density and viscosity data can provide a more complete thermophysical profile.
- Applying advanced modeling methods such as **Redlich–Kister polynomial fitting, Wilson, NRTL, and UNIQUAC equations of state**, can improve correlation of excess properties and predict non-ideal mixing behavior more accurately.
- Development of predictive software modules for solvent mixture behavior based on these models would benefit chemical engineers[17].
- Techniques such as **FTIR, Raman, and NMR spectroscopy** can be used to investigate molecular orientation and specific interaction sites between NMP and CCl₄ molecules.
- Spectroscopic data integrated with computational chemistry tools (e.g., DFT simulations) could quantify interaction energies and structural effects.

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