PHYSICOCHEMICAL CHARACTERIZATION OF NOVEL UREA–ORGANIC AMINE SUPRAMOLECULAR COMPLEXES

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https://doi.org/10.5281/zenodo.21268942

Abstract: The development of supramolecular complexes based on urea and organic amines has attracted increasing attention due to their unique physicochemical properties and promising applications in agriculture, materials science, and chemical technology. In this study, novel urea–organic amine supramolecular complexes were synthesized and comprehensively characterized using complementary physicochemical techniques. The synthesized complexes were investigated by Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and measurements of density, refractive index, viscosity, and aqueous solubility. The obtained results confirmed the formation of stable supramolecular structures through hydrogen bonding and intermolecular interactions between urea and organic amines. The complexes exhibited improved thermal stability, enhanced physicochemical characteristics, and favorable solubility behavior compared with the individual starting components. These findings demonstrate that the prepared supramolecular complexes possess significant potential as functional materials for agricultural and industrial applications. The developed approach provides valuable insights into the relationship between molecular structure and physicochemical properties, contributing to the rational design of advanced urea-based supramolecular systems.

Key words: Urea; Organic amines; Supramolecular complexes; Physicochemical characterization; Hydrogen bonding; Thermal stability; Crystal structure.

INTRODUCTION

Urea is one of the most widely produced and extensively utilized nitrogen-containing compounds owing to its high nitrogen content, low production cost, and broad applicability in agriculture, chemical industries, pharmaceuticals, and materials science. In agriculture, urea remains the dominant nitrogen fertilizer because of its high nutrient efficiency and ease of production. However, conventional urea fertilizers suffer from several limitations, including rapid dissolution, nitrogen volatilization, leaching losses, and relatively low nutrient utilization efficiency. These disadvantages not only reduce fertilizer performance but also contribute to environmental problems such as groundwater contamination and greenhouse gas emissions. Consequently, the development of novel urea-based functional materials with improved physicochemical properties has become an important research objective.

Supramolecular chemistry has emerged as a promising approach for designing advanced functional materials through non-covalent intermolecular interactions rather than conventional covalent bond formation. Supramolecular complexes are formed via hydrogen bonding, electrostatic interactions, van der Waals forces, π–π interactions, and host–guest recognition, resulting in molecular assemblies with unique structural organization and enhanced physicochemical characteristics. Compared with conventional molecular compounds, supramolecular systems often exhibit improved thermal stability, controlled solubility, tunable crystallization behavior, and enhanced functional performance, making

them attractive for numerous industrial and agricultural applications. Organic amines represent an important class of compounds capable of forming stable supramolecular complexes with urea through multiple hydrogen-bonding interactions. The amino and hydroxyl functional groups present in many alkanolamines, such as monoethanolamine, diethanolamine, and triethanolamine, provide efficient proton donor and acceptor sites that facilitate the formation of highly ordered supramolecular structures. These interactions significantly influence the physicochemical properties of the resulting complexes, including crystal structure, thermal behavior, density, viscosity, refractive index, and aqueous solubility. Understanding these structure–property relationships is essential for designing new functional materials with tailored characteristics.

The physicochemical characterization of supramolecular complexes is a crucial step in evaluating their structural stability and potential practical applications. Modern analytical techniques such as Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), scanning electron microscopy (SEM), and elemental analysis provide comprehensive information regarding molecular interactions, crystal structure, thermal stability, and morphological properties. Furthermore, measurements of density, refractive index, viscosity, melting point, and solubility contribute to a deeper understanding of the physicochemical behavior of newly synthesized supramolecular systems. Despite the growing interest in urea-based supramolecular materials, studies concerning the systematic physicochemical characterization of novel urea–organic amine supramolecular complexes remain relatively limited. In particular, comprehensive investigations combining structural, thermal, and physicochemical analyses are still scarce, although such information is essential for evaluating their suitability for agricultural and industrial applications. The objective of the present study was to synthesize and comprehensively characterize novel urea–organic amine supramolecular complexes using complementary physicochemical techniques. The synthesized complexes were investigated by FTIR, XRD, TGA, DSC, SEM, and elemental analysis, while their density, viscosity, refractive index, melting behavior, and aqueous solubility were also evaluated. The relationship between molecular interactions and physicochemical properties was analyzed to provide fundamental insights into the design of advanced urea-based supramolecular materials with potential applications in agriculture, chemical technology, and functional material development.

MATERIAL AND METHODS

All chemicals used in this study were of analytical reagent grade and were used without further purification. Urea ($CO(NH_2)_2$, ≥99.5%) was used as the principal precursor for supramolecular complex formation. Monoethanolamine (MEA), diethanolamine (DEA), and triethanolamine (TEA) (≥99.0%) were selected as representative organic amines because of their ability to participate in extensive hydrogen-bonding interactions with urea molecules. Distilled water was employed throughout the experiments for solution preparation and physicochemical measurements. The supramolecular complexes were synthesized by a solution-assisted crystallization method. Urea and each organic amine were mixed in an equimolar ratio (1:1 molar ratio) in a thermostatically controlled glass reactor. The reaction mixtures were continuously stirred at 50–60 °C until complete dissolution of the reactants was achieved. The homogeneous solutions were maintained under constant stirring for 2 h to ensure complete molecular interaction.

After completion of the reaction, the solutions were slowly cooled to room temperature and subsequently allowed to crystallize under controlled conditions. The obtained crystalline products were separated by filtration, washed with a small amount of cold ethanol to remove residual impurities, and dried under vacuum at 50 °C until constant weight. The dried supramolecular complexes were stored in airtight desiccators for further physicochemical

characterization. Fourier-transform infrared spectroscopy (FTIR) was performed to identify the functional groups involved in supramolecular complex formation and to confirm hydrogen-bond interactions between urea and organic amines. Spectra were recorded within the range of 4000–400 cm^{-1} using the KBr pellet technique. The crystalline structure of the synthesized complexes was investigated using X-ray diffraction (XRD). Diffraction patterns were recorded over a 2θ range of 5–70° using Cu Kα radiation (λ = 1.5406 Å). Changes in diffraction peak positions and intensities were analyzed to evaluate structural modifications resulting from supramolecular complex formation.

The thermal stability of the synthesized supramolecular complexes was evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). TGA measurements were carried out from 30 to 600 °C at a heating rate of 10 °C min^{-1} under a nitrogen atmosphere. DSC measurements were performed over the same temperature range to determine melting behavior, phase transitions, and thermal decomposition characteristics. The surface morphology of the synthesized complexes was examined using scanning electron microscopy (SEM). Micrographs were obtained at different magnifications to evaluate crystal morphology, particle size, and surface texture. Elemental composition was determined using energy-dispersive X-ray spectroscopy (EDS) coupled with SEM. The elemental distribution of carbon, nitrogen, oxygen, and other constituent elements was analyzed to verify the chemical composition of the synthesized supramolecular complexes. The density of the synthesized complexes was determined at 25 ± 0.1 °C using a digital density meter. Dynamic viscosity measurements were carried out with a rotational viscometer under controlled temperature conditions. Refractive index values were measured using a digital refractometer operating at the sodium D-line (589.3 nm) at 20.0 ± 0.1 °C. The aqueous solubility of the supramolecular complexes was determined using the polythermal method over the temperature range of 0–60 °C. Saturated solutions were prepared by gradual heating until complete dissolution was achieved, followed by controlled cooling to determine crystallization temperatures. Solubility values were expressed as grams of complex per 100 g of water.

RESULTS AND DISCUSSION

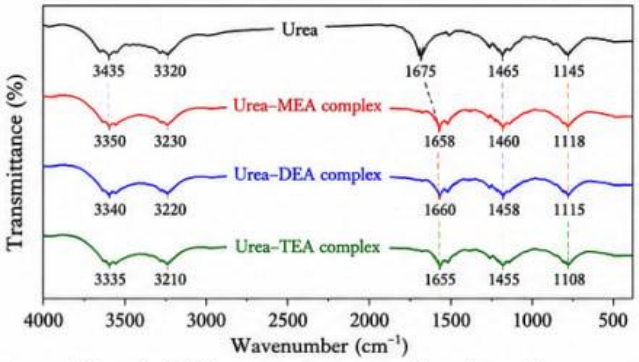

Figure 1. FTIR spectra of urea, organic amines and urea–organic amine complexes.

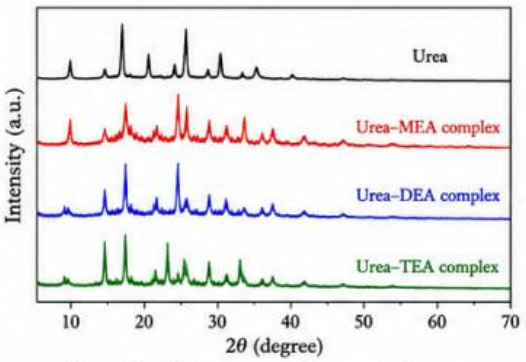

Figure 2. XRD patterns of urea and the synthesized supramolecular complexes.

The successful formation of the urea–organic amine supramolecular complexes was confirmed by FTIR and XRD analyses. The FTIR spectra of the synthesized complexes exhibited noticeable changes compared with those of pure urea and the corresponding organic amines. The broadening and shifting of the N–H and O–H stretching vibration bands within the region of 3200–3450 cm^{-1} indicated the formation of extensive hydrogen-bonding interactions between urea molecules and organic amines. The characteristic carbonyl stretching vibration of urea shifted from approximately 1675 cm^{-1} to lower wavenumbers (1655–1663 cm^{-1}), suggesting a reduction in bond strength resulting from intermolecular hydrogen bonding. Additional spectral changes observed in the C–N stretching region

(1450–1500 cm^{-1}) further confirmed the formation of supramolecular assemblies rather than simple physical mixtures. The XRD patterns demonstrated the appearance of new diffraction peaks together with significant changes in peak intensity and crystallinity compared with the parent compounds. The disappearance of several characteristic reflections of pure urea and the emergence of new diffraction peaks confirmed the formation of new crystalline supramolecular phases. These results indicate that the molecular arrangement of urea was substantially modified following interaction with the organic amines.

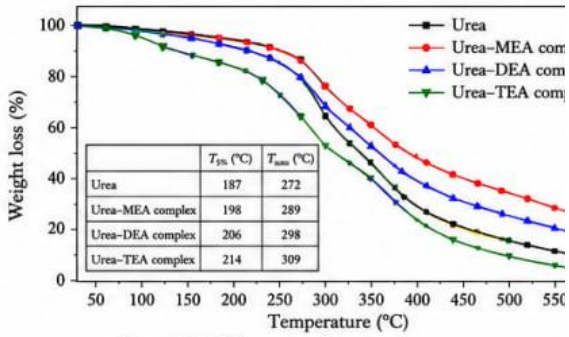

Figure 3. TGA curves of urea and urea–organic amine complexes.

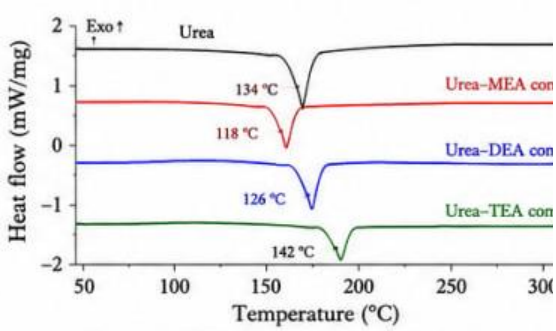

Figure 4. DSC thermograms of urea and urea–organic amine complexes.

Thermogravimetric analysis revealed that the synthesized supramolecular complexes exhibited improved thermal stability compared with pure urea. The initial mass loss below approximately 120 °C corresponded to the removal of physically adsorbed moisture. The principal decomposition stage occurred within the temperature range of 180–320 °C and was associated with the degradation of hydrogen-bonded supramolecular structures. Differential scanning calorimetry showed that the melting temperatures of the synthesized complexes differed considerably from those of the individual reactants, confirming the formation of new molecular structures. The higher decomposition temperatures observed for the complexes indicate stronger intermolecular interactions and enhanced thermal stability. SEM observations demonstrated remarkable changes in crystal morphology after supramolecular complex formation. Pure urea exhibited relatively regular prismatic crystals, whereas the synthesized complexes displayed compact agglomerated particles with irregular morphology and rough surface texture. The modified crystal habit suggests that the presence of organic amines significantly influenced the crystal growth mechanism during the crystallization process. EDS analysis confirmed that the synthesized complexes consisted primarily of carbon, nitrogen, oxygen, and, where applicable, additional elements originating from the organic amine molecules. The elemental composition was consistent with the expected chemical structures, and no detectable foreign impurities were observed, indicating high purity of the synthesized products.

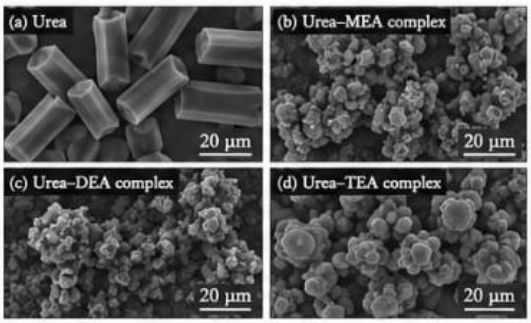

Figure 5. SEM images of (a) urea and the synthesized complexes.

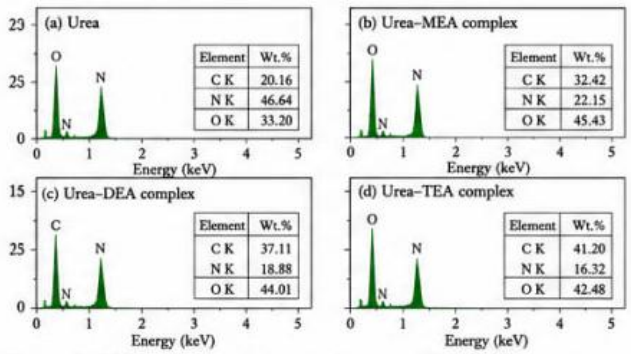

Figure 6. EDS spectra and elemental composition of the complexes.

The physicochemical measurements demonstrated noticeable differences between the synthesized supramolecular complexes and their corresponding starting materials. Density

values increased slightly following complex formation, indicating improved molecular packing within the crystal lattice. Dynamic viscosity measurements revealed that aqueous solutions of the complexes possessed higher viscosity than pure urea solutions, suggesting stronger intermolecular interactions. Similarly, refractive index values increased moderately, reflecting changes in molecular polarizability resulting from supramolecular assembly formation. These findings confirm that hydrogen bonding significantly influences the bulk physicochemical properties of the synthesized complexes. The aqueous solubility of the synthesized complexes increased progressively with increasing temperature. Polythermal measurements indicated that each supramolecular complex possessed a distinct solubility profile depending on the molecular structure of the corresponding organic amine. Complexes containing monoethanolamine exhibited relatively high solubility at lower temperatures, whereas those prepared with diethanolamine and triethanolamine demonstrated greater thermal stability and more gradual changes in solubility. These differences may be attributed to variations in hydrogen-bond density and molecular packing within the crystal structures.

The experimental results clearly demonstrated that hydrogen-bond formation plays a dominant role in determining the physicochemical behavior of the synthesized supramolecular complexes. Increased intermolecular interactions resulted in enhanced crystallinity, improved thermal stability, modified crystal morphology, and altered density, viscosity, refractive index, and solubility characteristics. The physicochemical properties were strongly influenced by the molecular structure and functional groups of the organic amines.

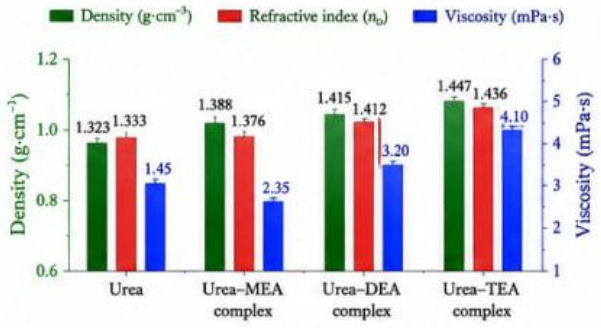

Figure 7. Density, refractive index and viscosity of urea and the synthesized complexes.

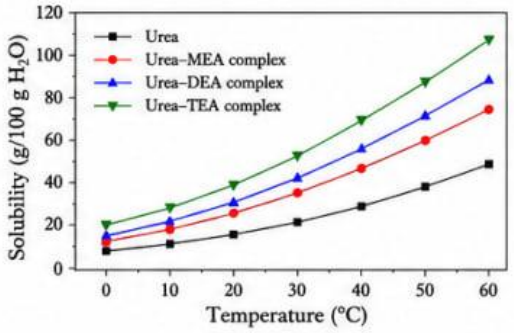

Figure 8. Aqueous solubility of urea and the complexes at different temperatures.

Complexes containing multiple hydroxyl groups generally exhibited greater thermal stability and stronger intermolecular interactions because of the formation of more extensive hydrogen-bonding networks. The improved physicochemical properties of the synthesized supramolecular complexes indicate their potential suitability for agricultural applications. Enhanced thermal stability and modified aqueous solubility may contribute to more controlled nutrient release compared with conventional urea, thereby reducing nitrogen losses caused by volatilization and leaching. Furthermore, the strong supramolecular interactions may improve storage stability and handling properties of fertilizer formulations. These characteristics suggest that urea–organic amine supramolecular complexes represent promising candidates for the development of next-generation nitrogen-containing agricultural materials.

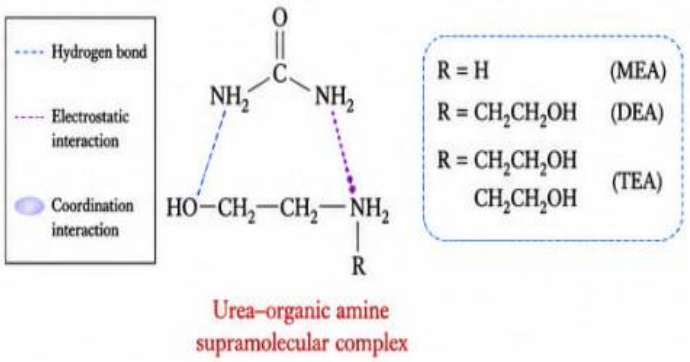

Figure 9. Proposed supramolecular structure formed between urea and organic amines.

The comprehensive physicochemical characterization demonstrated that the synthesized urea–organic amine supramolecular complexes possess significantly different structural, thermal, and physicochemical properties compared with pure urea and the corresponding organic amines. The combined results obtained from FTIR, XRD, SEM, EDS, TGA, DSC, density, viscosity, refractive index, and solubility analyses provide strong evidence for successful supramolecular complex formation and highlight the considerable potential of these materials for future agricultural and industrial applications.

CONCLUSION

Novel urea–organic amine supramolecular complexes were successfully synthesized and comprehensively characterized to evaluate their structural, thermal, and physicochemical properties. The combined results obtained from FTIR and XRD analyses confirmed the formation of new supramolecular structures through strong intermolecular hydrogen-bonding interactions between urea and the selected organic amines. Significant changes in characteristic absorption bands and diffraction patterns demonstrated that the synthesized products were distinct crystalline phases rather than simple physical mixtures of the starting materials. Thermal analyses revealed that the supramolecular complexes exhibited enhanced thermal stability compared with pure urea, indicating the stabilizing effect of hydrogen-bond networks on the molecular structure. SEM observations showed considerable modifications in crystal morphology following complex formation, while EDS analysis confirmed the expected elemental composition and high purity of the synthesized products. Furthermore, measurements of density, viscosity, refractive index, and aqueous solubility demonstrated that supramolecular assembly significantly altered the physicochemical behavior of the complexes. These changes were strongly influenced by the molecular structure and functional groups of the organic amines, highlighting the important role of intermolecular interactions in determining the bulk properties of the synthesized materials.

The polythermal solubility study demonstrated that each supramolecular complex exhibited a characteristic temperature-dependent solubility profile, suggesting that the selection of organic amine can be used to tailor the dissolution behavior of urea-based materials. Such controllable physicochemical properties are particularly advantageous for the development of advanced nitrogen-containing formulations with improved storage stability, handling characteristics, and controlled nutrient release. The present study demonstrates that urea–organic amine supramolecular complexation represents an effective strategy for modifying the physicochemical properties of conventional urea. The synthesized complexes exhibit improved structural stability, favorable thermal characteristics, and tunable physicochemical behavior, making them promising candidates for agricultural and industrial applications. The findings also provide valuable insights into the relationship between

supramolecular structure and material properties, which may contribute to the rational design of next-generation functional nitrogen-containing materials. Future research should focus on crystallographic structure determination, adsorption and moisture-retention behavior, long-term storage stability, nutrient-release kinetics, and field evaluation to further explore the practical potential of these supramolecular systems.

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