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Dissolution Behavior of Polysaccharides in Choline Chloride-Based Deep Eutectic Solvents: A Comparative Study of Urea and Oxalic Acid Systems

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Abstract

Polysaccharides are essential biopolymers composed of long chains of monosaccharide units linked by glycosidic bonds, serving both structural and storage functions in biological systems. Representative polysaccharides such as cellulose, chitin, chitosan, and alginate possess distinct physicochemical properties and industrial relevance. Cellulose, a *β*-D-glucose polymer, forms rigid plant cell walls and is resistant to dissolution due to extensive hydrogen bonding. Chitin, present in arthropod exoskeletons and fungal cell walls, and its derivative chitosan offer broad biomedical applications. Alginate, derived from brown seaweed, is appreciated for its gel-forming capacity and biocompatibility. However, the strong hydrogen bonding networks in these polysaccharides hinder their solubility in conventional solvents, necessitating harsh chemical or physical treatment, which is often environmentally and economically unsustainable. Deep eutectic solvents (DES), formed by mixing a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA), have emerged as a green and cost-effective alternative for polysaccharide processing. These solvents disrupt internal hydrogen bonding through intermolecular interactions, enhancing solubility while preserving structural integrity. This study investigates the dissolution behavior of various polysaccharides in DES systems based on choline chloride combined with urea (CCU) or oxalic acid (COA), with a focus on optimizing parameters such as temperature, component ratio, and HBD type. Dissolution efficiency was evaluated gravimetrically, and ATR-FTIR spectroscopy was used to assess structural changes and interactions. Results revealed that cellulose dissolution in CCU is optimal at temperatures below 90 °C, while temperatures above 100°C promote carbamation, inhibiting dissolution. Conversely, the COA system induced structural modifications even below 100°C, suggesting stronger reactivity. Overall, choline chloride/urea (ChCl/urea) showed more favorable, non-destructive interactions, indicating its potential as a more suitable DES for polysaccharide dissolution.

Keywords Deep eutectic solvent; choline chloride; urea; oxalic acid; cellulose; chitosan; alginate; polysaccharide dissolution

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1.0 INTRODUCTION

Polysaccharides are high-molecular-weight carbohydrates composed of repeating monosaccharide units linked through glycosidic bonds. They fulfill essential biological functions and are broadly classified into structural and storage polysaccharides. Among the most extensively studied structural polysaccharides are cellulose, chitin, chitosan, and alginate, each exhibiting distinct physicochemical properties and functional potential.

Cellulose is a linear homopolysaccharide consisting of *β*-D-glucopyranose units, and its rigid, fibrous architecture contributes to the mechanical strength of plant cell walls. The extensive network of inter- and intramolecular hydrogen bonding renders cellulose highly crystalline, insoluble in water, and resistant to enzymatic hydrolysis, thereby posing significant challenges for its dissolution and subsequent processing [1]. Chitin, composed of *N*-acetyl-D-glucosamine units, is the primary structural component of arthropod exoskeletons and fungal cell walls. Its deacetylated derivative, chitosan, exhibits improved solubility under mildly acidic conditions while retaining desirable biological properties, facilitating its application in biomedicine, agriculture, and environmental remediation [2]. Alginate, an anionic polysaccharide extracted from brown macroalgae, consists of (1→4)-linked *β*-D-mannuronic acid and *α*-L-guluronic acid residues. Moreover, Alginate has the ability to form hydrogels in the presence of divalent cations and its excellent biocompatibility make it particularly attractive for biomedical applications, including controlled drug delivery and tissue engineering [3].

Despite their potential, the processing and functionalization of polysaccharides are often hindered by their extensive hydrogen bonding networks, which confer high thermal and chemical stability but significantly limit solubility in conventional solvents [4]. For instance, cellulose dissolution typically requires aggressive chemical treatments or high-energy physical methods, which are often economically and environmentally unsustainable.

In recent years, deep eutectic solvents (DES) have emerged as a promising class of green solvents, offering a safer, more sustainable, and cost-effective alternative to traditional organic solvents and ionic liquids for the dissolution of polysaccharides. DES are typically formed by complexation between a hydrogen bond acceptor (HBA) and a hydrogen bond donor (HBD), resulting in a eutectic mixture with a melting point significantly lower than that of the individual components. This unique property enables DES to effectively disrupt the hydrogen bonding networks within polysaccharides, thereby enhancing their solubility [5]. The proposed dissolution mechanism involves the formation of new hydrogen bonds between the DES constituents and polysaccharide chains, weakening the internal hydrogen bonding and facilitating molecular dispersion. Moreover, DES can preserve the structural integrity and functional groups of the polysaccharides, making them particularly attractive for applications in materials science, catalysis, and biotechnology [6].

The main objective of this study is to enhance the synthesis and performance of DES based on choline chloride (ChCl) with urea and oxalic acid (OA) as HBDs. The focus is on optimizing their physicochemical properties; including solvating power, dissolution capacity, and recyclability; for improved interaction with polysaccharides. The effects of HBD type, molar ratio, and processing temperature on polysaccharide dissolution and reaction kinetics will be systematically investigated to establish structure, property relationships, and inform the rational design of efficient DES systems.

2.0 EXPERIMENTAL

2.1 Materials

ChCl (99%, AR grade), urea (99%, AR grade), and OA (≥99%, AR grade) were purchased from Chemiz (Selangor, MY). Meanwhile, microcrystalline cellulose (MCC), chitin, chitosan, alginate, and starch were purchased from Sigma-Aldrich (Missouri, US). All chemicals were used as received without further purification.

2.2 Preparation of ChCl/Urea DES and ChCl/OA DES

DES were prepared by mixing ChCl (20.0 g, 0.167 mol) with urea (40.0 g, 0.667 mol) or OA (40.0 g, 0.444 mol) at the specified molar ratios. All reagents were pre-dried in a vacuum oven at 50°C for 6 hours to reduce the moisture content significantly. Following this initial drying, any remaining residual moisture was eliminated by heating the reagents at a constant temperature for 30 minutes. Each mixture was transferred into a four-necked round-bottom flask, placed in an oil bath, and stirred at 80 °C for 1 hour until a homogeneous, clear solution was obtained. The DES was then cooled to room temperature and stored in a desiccator for later use.

2.3 Dissolution of Microcrystalline Cellulose in ChCl/Urea DES

The dissolution procedure for MCC was adapted from Zhang et al. [7]. MCC (0.2 g) was added to a reaction vial, and the corresponding ChCl/urea DES was added at different weight ratios: 1:5, 1:10, 1:15, and 1:20 (MCC:DES). For example, a 1:10 ratio corresponds to 2.0 g of DES added to 0.2 g of MCC. The mixture was heated in an oil bath at 80°C, 90°C, or 100°C for 3 hours. After the reaction, the mixture was washed with distilled water, filtered, and dried at 75°C. The dried residue was then weighed to determine the mass difference. Dissolution efficiency was calculated using the following equation:

$$\frac{(M-Mc)}{M} \times 100$$

where M and Mc are the initial weight and dried reacted compound weight, respectively.

2.4 Attenuated Total Reflectance – Fourier Transform Infrared (ATR-FTIR) Spectroscopy

ATR-FTIR was performed to analyze the functional group of polysaccharides using a Perkin Elmer spectrometer and ATR accessory, accumulating 32 scans in 4000-600 cm^{-1} range. Appropriate amounts of the samples were placed directly onto the ATR crystal for measurement.

3.0 RESULTS AND DISCUSSION

3.1 ATR-FTIR Spectra of Cellulose in DES CCU

ATR-FTIR spectra for cellulose (**Figure 1 (a)**) reacted with CCU DES at 80°C and 90°C show no distinct peaks corresponding to the components of DES, such as the C=O and N-H stretching of urea or the C-H stretching of ChCl, in the cellulose/DES CCU mixtures. This indicates that the cellulose obtained is pure and free from DES contamination, exhibits successful removal of DES components, and leaves behind clean cellulose. In another case, as observed in **Figure 1 (b)**, cellulose reacted in CCU DES at 100°C shows a significant peak at 1500 to 1700 cm^{-1}, indicating the presence of a C=O functional group. Cellulose reacted with urea from CCU DES through the carbamation process [8]. This is only observed when cellulose is reacted in CCU DES at 100°C. The CCU DES remained inert at a temperature lower than 100°C, facilitating the dissolution of cellulose. This is new theoretically.

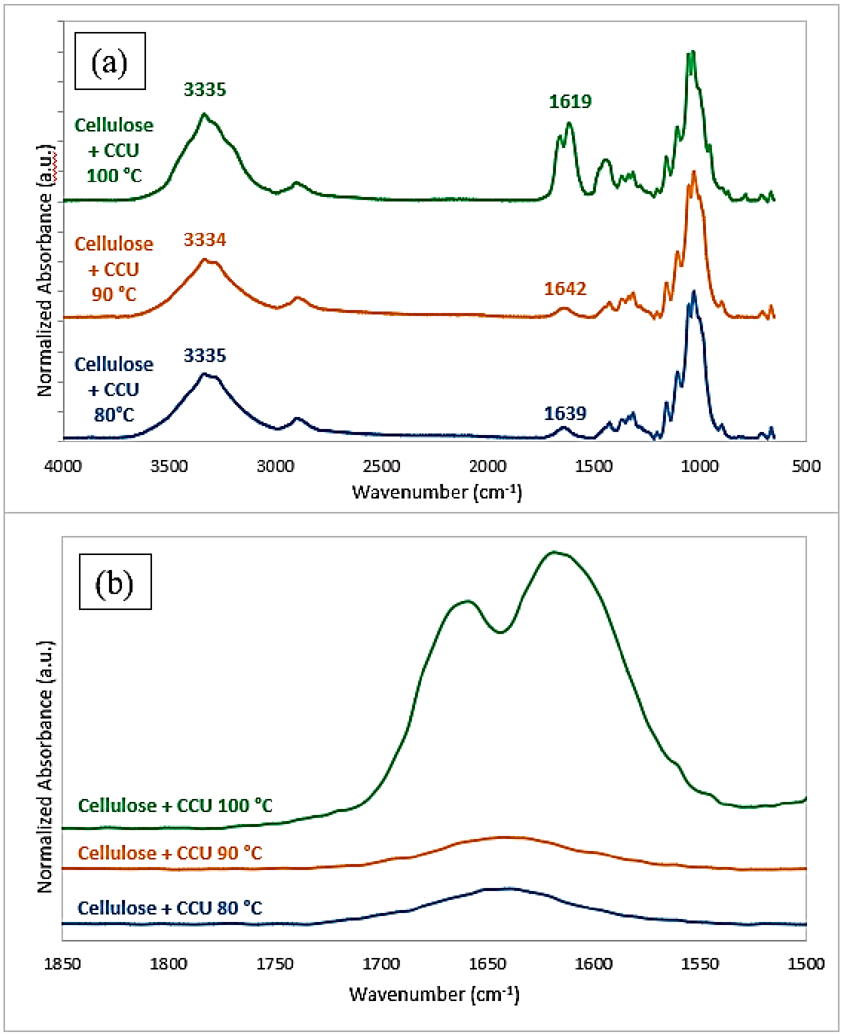

Figure 1 ATR-FTIR Spectra of Cellulose in (a) DES CCU at 100°C compared to 80°C and 90°C (b) magnified view at 1850–1500 cm^{-1}

3.2 Characterization of Chitin in DES CCU and DES COA

ATR-FTIR spectra of chitin (**Figure 2**) with DES CCU and DES COA at 90°C reveal distinct interactions. The O-H stretching peak at 3397.29 cm^{-1} for chitin/DES CCU indicates strong hydrogen bonding between chitin and DES CCU, with the higher wavenumber suggesting less involvement of O-H groups in bonding with the solvent. Otherwise, the O-H peak at 3336.33

cm⁻¹ for chitin/DES COA indicates more extensive hydrogen bonding due to the acidic nature of OA. The C-H stretching peak at 2924.72 cm⁻¹ for chitin/DES CCU shows less disruption of the chitin structure, while the lower peak at 2899.89 cm⁻¹ for chitin/DES COA suggests stronger interactions with the aliphatic C-H groups, likely due to the acidic component.

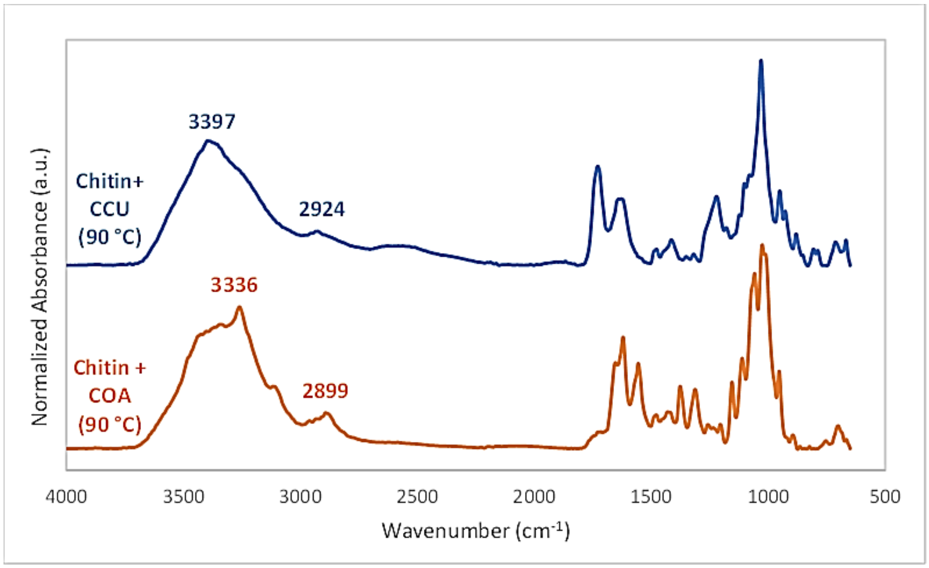

Figure 2 ATR-FTIR spectra of chitin in DES CCU and COA at 90°C

3.3 Characterization of Chitosan in DES CCU and DES COA

ATR-FTIR spectra of chitosan (**Figure 3**) with DES COA (1:15 molar ratio) are presented, showing distinct peaks for O-H and C-H stretches. The O-H stretch for chitosan/DES is observed at 3349.71 cm⁻¹, and for DES COA at 3338.35 cm⁻¹, while the C-H stretch is at 2939.09 cm⁻¹ for chitosan/DES and 2959.18 cm⁻¹ for DES COA. These peaks indicate the interaction between the chitosan and the DES components, revealing how the hydrogen bonding and molecular interactions influence the spectral features.

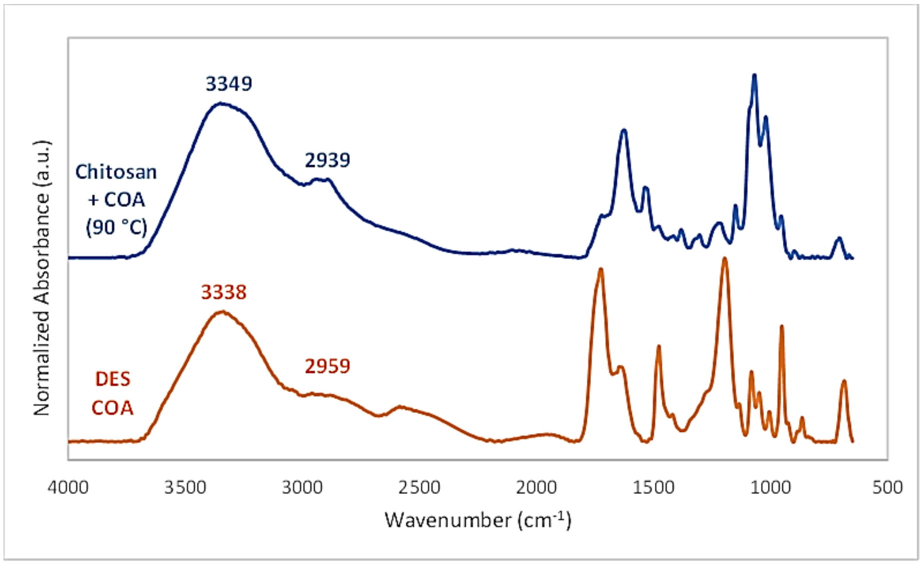

Figure 3 ATR-FTIR spectra of chitosan in DES COA and DES COA as reference at 90°C

3.4 Characterization of Alginate in DES CCU and DES COA

ATR-FTIR spectra of alginate (**Figure 4**) with DES CCU and DES COA under the same conditions. The spectrum highlights the O-H stretches at 3348.14 cm⁻¹ for alginate/DES CCU and 3401.92 cm⁻¹ for DES COA, with a notable peak at 2918.28 cm⁻¹ for the C-H stretch in DES COA. The appearance of these peaks is significant as it indicates the presence of strong hydrogen bonding and van der Waals interactions between the alginate and the DES components. The peaks are the result of the molecular vibrations of the functional groups, which are enhanced due to the DES's ability to disrupt the original bonding in alginate, leading to new interaction patterns [9].

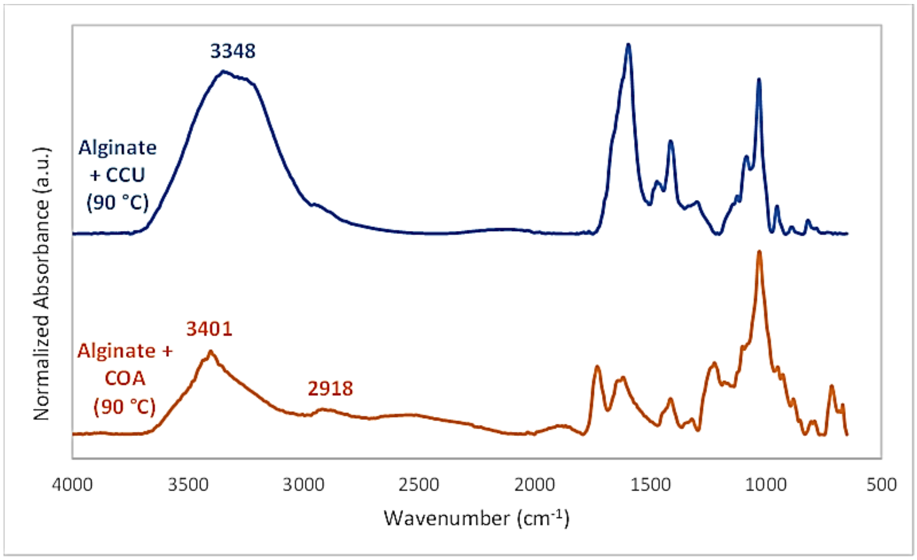

Figure 4 ATR-FTIR spectra of alginate in DES CCU and COA at 90°C

4.0 CONCLUSION

This research study has shown the dissolution of polysaccharides in ChCl-based DES for cellulose, chitin, chitosan, and alginate. It was found that ChCl/Urea DES was highly effective in breaking down the hydrogen bonds within the polysaccharides, leading to significant dissolution in the reacted products. For instance, cellulose exhibited high solubility in CCU DES due to the solvent's strong hydrogen bonding capabilities and lower melting point, facilitating better penetration into the cellulose structure. Chitosan and alginate also dissolved efficiently in DES without major structural changes, demonstrating the potential of these solvents to enhance polysaccharide processing. These findings suggest that DES can serve as an eco-friendly and efficient solvent for the industrial processing of polysaccharides, offering a sustainable alternative to traditional methods. Overall, the use of ChCl-based DES has been proven to enhance the dissolution of various polysaccharides, with ChCl/Urea DES showing a higher potential than ChCl/Oxalic Acid DES as a solvent.

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