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CHOLINE CHLORIDE BASED DEEP EUTECTIC SOLVENTS: PHYSICOCHEMICAL PROPERTIES AND SPECTROSCOPIC INSIGHTS

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ABSTRAK

Penelitian ini berfokus pada sintesis dan karakterisasi Deep Eutectic Solvents (DES) berbasis Choline Chloride dengan menggunakan Asam Sitrat (ChCl+CA) dan Asam Malat (ChCl+MA) sebagai donor ikatan hidrogen. DES disintesis pada berbagai rasio molar, dan sifat fisikokimia mereka, termasuk viskositas, densitas, pH, kadar air, serta interaksi molekular, dianalisis secara komprehensif. Analisis spektroskopi FTIR menunjukkan pergeseran signifikan pada gugus fungsional, yang mengindikasikan adanya ikatan hidrogen yang kuat antara komponen-komponen DES. Meskipun ChCl+CA dan ChCl+MA berhasil membentuk pelarut eutektik yang stabil pada rasio molar 1:1, sintesis dengan rasio molar yang lebih tinggi (1:2 dan 1:3) serta ChCl+Ethylene Glycol (ChCl+EG) tidak berhasil, yang menekankan pentingnya kompatibilitas komponen dan rasio molar. Pengukuran densitas dan viskositas menunjukkan potensi penerapan DES ini dalam proses ekstraksi. Penelitian ini berkontribusi pada pengembangan DES sebagai pelarut ramah lingkungan, dengan aplikasi di masa depan dalam ekstraksi pigmen untuk keperluan kosmetik.

Kata kunci: Deep Eutectic Solvents, Choline Chloride, Asam Sitrat, Asam Malat, Ekstraksi Pigmen, Aplikasi Kosmetik

ABSTRACT

This study focuses on the synthesis and characterization of Choline Chloride-based Deep Eutectic Solvents (DES) using Citric Acid (ChCl+CA) and Malic Acid (ChCl+MA) as hydrogen bond donors. The DES were prepared at various molar ratios, and their physicochemical properties, including viscosity, density, pH, water content, and molecular interactions, were comprehensively analyzed. The FTIR spectroscopic analysis revealed key shifts in the functional groups, indicating strong hydrogen bonding between the DES components. While ChCl+CA and ChCl+MA successfully formed stable eutectic solvents at a 1:1 molar ratio, synthesis with higher molar ratios (1:2 and 1:3) and ChCl+Ethylene Glycol (ChCl+EG) were unsuccessful, highlighting the importance of component compatibility and molar ratios. The density and viscosity measurements showed the potential applicability of these DES in extraction processes. This research contributes to the development of DES as green solvents, with future applications in pigment extraction for cosmetic purposes.

Keywords: Deep Eutectic Solvents, Choline Chloride, Citric Acid, Malic Acid, Pigment Extraction, Cosmetic Applications

INTRODUCTION

The widespread use of traditional organic solvents in industrial and laboratory processes has long posed environmental and health hazards. Solvents like chlorinated hydrocarbons and volatile organic compounds (VOCs) are toxic, flammable, and non-biodegradable, contributing significantly to air and water pollution (Grotto et al., 2009). These solvents also endanger workers' health due to their volatility, resulting in inhalation risks and concerns over prolonged exposure. Additionally, their disposal creates hazardous waste, increasing both environmental strain and operational costs (Okoro et al., 2023). Historically, the chemical industry heavily depended on these solvents for efficient chemical reactions, extractions, and separations. However, with stricter environmental regulations and a shift toward sustainable practices, alternatives such as ionic liquids (ILs) emerged in the late 20th century. Although ILs have low volatility and adjustable properties, issues around cost, toxicity, and environmental persistence have limited their broader adoption (Hijo et al., 2016).

Recently, Deep Eutectic Solvents (DES) have shown promise as a green solvent alternative (Turiel, 2023). DES are mixtures of a hydrogen bond acceptor (HBA) and a hydrogen bond donor (HBD) in specific ratios, resulting in a lower melting point than their individual components. This decrease is due to strong hydrogen bonding and electrostatic interactions, making DES typically liquid at room temperature. DES offer flexibility through customizable HBA and HBD combinations, enabling control over properties like viscosity, solubility, and polarity (Pereira et al., 2013). Unlike traditional solvents, DES are usually biodegradable and less toxic, often sourced from natural components like choline chloride and organic acids, and have low volatility, reducing VOC emissions. This versatility suits applications from chemical synthesis to biocatalysis and extraction (Buarque et al., 2022). For example, DES have proven effective in extracting anthocyanins, valuable antioxidants and colorants for food and pharmaceutical uses, offering a sustainable alternative to toxic solvents typically used for such extractions (Cunha et al., 2018).

Despite their benefits, DES have limitations. Their relatively high viscosity can hinder applications needing rapid mass transfer, and the biodegradability of some DES formulations is still under study. Challenges with scalability and economic viability remain for large-scale industrial use. Therefore, thorough characterization of DES is essential to optimize their applications in various fields. This involves analyzing properties such as viscosity, water content,

pH, and molecular interactions using techniques like FTIR spectroscopy, which provides insights into functional group interactions critical for tailoring DES properties (Achkar, 2021). Viscosity, for example, affects mass transfer rates in extractions, while water content can impact the solvent's effectiveness and stability. Understanding pH is important in environments sensitive to pH changes, and FTIR aids in identifying structural features that influence DES behavior.

This study specifically focuses on characterizing choline chloride-based DES, examining viscosity, water content, pH, and FTIR spectroscopic properties. These parameters are vital for evaluating DES practicality in various industries and assessing their potential to replace conventional, hazardous solvents with greener, more sustainable options.

METHODS

Tools and Materials

The materials that were used are malic acid was purchased from Merck, choline chloride, Hi-LR were purchased from Himedia. Technical grade citric acid and ethylen glycol.

Procedure

Preparation of Deep Eutectic Solvents (DES)

Synthesize of DES, based on previous research (Achkar, et.al, 2021) with modification. Three types of deep eutectic solvents (DES) were synthesized for this study: Choline Chloride-Citric Acid (ChCl+CA), Choline Chloride-Malic Acid (ChCl+MA), and Choline Chloride-Ethylene Glycol (ChCl+EG). The preparation of each DES followed a consistent method based on molar ratios of 1:1, 1:2, and 1:3 between the hydrogen bond acceptor (HBA) and hydrogen bond donor (HBD).

For each DES, the corresponding amounts of choline chloride (HBA) and either citric acid, malic acid, or ethylene glycol (HBD) were mixed in the specified molar ratios. The mixture was heated at 60-70°C under atmospheric pressure while being stirred continuously. The stirring process was maintained until a homogeneous and stable liquid was formed. The resulting DES was then allowed to cool to room temperature before use in subsequent analyses.

Characterization of DES

Density Measurement

Density was measured using a pycnometer. The device was filled with the DES sample, weighed, and temperature was maintained at 25°C. Density calculations were made using mass and volume data from the pycnometer.

Viscosity Measurement

Viscosity was determined using a viscometer at 25°C. Samples were equilibrated at temperature before viscosity was measured in centipoise (cP).

pH Measurement

The pH of each DES was measured using pH indicator papers due to the simplicity and rapid assessment they offer. This method was suitable for quickly gauging the acidity or neutrality of the DES samples at room temperature.

Water Content Measurement

Water content was determined by a gravimetric method. Approximately 1 gram of each DES was placed in a pre-heated vial at 105°C for 30 minutes to dry. The sample was then cooled in a desiccator for 15 minutes and weighed. This process was repeated until a constant weight (with a difference of less than 0.002 grams) was achieved.

FTIR Analysis

Fourier Transform Infrared Spectroscopy (FTIR) was employed to characterize the molecular interactions and chemical structure of the DES. Samples were prepared by mixing a small quantity of each DES with potassium bromide (KBr) and pressing the mixture into pellets. FTIR spectra were recorded in the range of 4000 to 400 cm^-1 using a KBr pellet method.

RESULT AND DISCUSSION

Preparation of Deep Eutectic Solvents (DES)

The experimental synthesis of deep eutectic solvents (DES) was conducted using Choline Chloride (ChCl) as a common hydrogen bond acceptor paired with three different hydrogen bond donors: Citric Acid (CA), Malic Acid (MA), and Ethylene Glycol (EG), at various molar ratios.mixture does not maintain a liquid state under the conditions tested.

The synthesis of ChCl+CA and ChCl+MA DES at a 1:1 molar ratio resulted in the successful formation of clear, homogeneous liquids, indicative of effective eutectic interactions

(Figure 1). The mixtures achieved a stable liquid state upon heating to 60-70°C with continuous stirring, confirming the strong hydrogen bonding capabilities of CA and MA with ChCl. This success demonstrates the potential of these DES compositions for various applications requiring biodegradable and low-toxicity solvents.

Conversely, the ChCl+EG combination at a 1:1 molar ratio did not result in a stable liquid phase. Despite similar conditions applied, the mixture failed to transition beyond a viscous slurry, suggesting inadequate interactions between ChCl and EG to form a true deep eutectic solvent at this ratio. This outcome highlights the need for further optimization, possibly exploring different temperature profiles, molar ratios, or mechanical stirring intensities to facilitate a successful eutectic formation.

Figure 1. Result of the succeed DES synthesize

Further attempts to synthesize all three types of DES at higher molar ratios of 1:2 and 1:3 uniformly resulted in failures. These ratios did not yield stable liquid phases under the conditions tested. The increasing proportion of the hydrogen bond donors compared to ChCl likely disrupts the delicate balance required for effective eutectic formation. The absence of a liquid phase at these higher ratios points to a critical limitation in the solvation capacity of ChCl when excessively diluted by the donors, necessitating a reevaluation of the component ratios or the introduction of additives to stabilize the mixture.

The mixed outcomes of this study underscore the complexity of DES synthesis, where the nature of the components and their proportions critically determine the success of the solvent formation. Particularly, the failure of higher molar ratios and the ChCl+EG system at a 1:1 ratio suggests that not all potential DES combinations are viable under standard conditions. These findings direct future research towards refining the synthesis parameters and exploring broader

conditions that may enable successful DES formation across a wider range of component ratios and types.

Characterization of DES

Density Measurement

The density differences between Choline Chloride-Citric Acid (ChCl+CA) and Choline Chloride-Malic Acid (ChCl+MA) reflect the distinct interactions and molecular arrangements driven by the carboxylic groups of the hydrogen bond donors, which influence their physical properties and industrial suitability, especially in extraction processes (Dai, 2012). ChCl+CA has a higher density of 1.4482 g/mL, suggesting a more tightly packed molecular structure that may enhance its ability to dissolve and interact with denser organic compounds. This is particularly useful in extraction processes where solvent density and solubility impact solute recovery efficiency, such as in extracting lipophilic substances from biological matrices in pharmaceutical and food industries (Maity et al., 2020; Maaiden, 2023).

In contrast, ChCl+MA, with a density of 1.40285 g/mL, exhibits a slightly lower density, which may lead to different interactions with target compounds. Its less dense structure, influenced by malic acid, might make it more suitable for extracting less dense or more polar compounds compared to ChCl+CA. This solvent is potentially effective in applications requiring balanced hydrophilicity, such as the extraction of flavonoids or polyphenolic compounds, which need solvents that can penetrate plant cells and ensure efficient extraction. The higher density of ChCl+CA is attributed to the increased hydrogen bonding in its system, leading to a more compact molecular structure (Gholami & Roosta, 2020).

Viscosity Measurement

Viscosity measurements of the synthesized deep eutectic solvents (DES) were conducted using a viscometer at 30 RPM, with ChCl+CA exhibiting a viscosity of 12,869 mPa·s at 64.3% torque, and ChCl+MA having a viscosity of 7,026 mPa·s at 35.1% torque. The significant difference in viscosity is attributed to the molecular structures and hydrogen bonding networks in each DES. ChCl+CA's higher viscosity is due to the polyfunctional citric acid, which forms a dense hydrogen bonding network, restricting molecular mobility and increasing internal friction, as reflected in the high torque required for measurement. This makes ChCl+CA less suitable for rapid mass transfer applications but beneficial for systems requiring solvent stability, like controlled release or catalytic reactions (Lomba, 2023).

On the other hand, the lower viscosity of ChCl+MA is due to the less extensive hydrogen bonding in malic acid, resulting in higher molecular mobility and lower resistance to flow. This makes ChCl+MA more suitable for processes requiring efficient mass transfer, such as liquid-liquid extractions, where faster solute penetration is beneficial. The viscosity also plays a critical role in determining a solvent's suitability for extraction processes. Highly viscous solvents, like ChCl+CA, may reduce mass transfer efficiency, while ChCl+MA's lower viscosity enhances solute diffusion, making it more effective for solid-liquid extractions (Biernacki, 2020).

The viscosity of a DES is also influenced by the molecular weight and structure of the hydrogen bond donor, with larger, more complex molecules increasing viscosity due to steric hindrance (Biernacki et al., 2020). Additionally, van der Waals forces, in combination with hydrogen bonding, can further increase viscosity by enhancing solvent cohesion (Tan, 2024). Temperature also plays a crucial role, as increased temperature typically reduces viscosity by providing molecules with more kinetic energy, a factor to consider in temperature-sensitive processes (Taysun, 2017).

pH Measurment

The pH results of ChCl+CA and ChCl+MA, both at pH 1, confirm the strong acidic environment created by the use of citric acid and malic acid as hydrogen bond donors (HBDs) in combination with choline chloride. This highly acidic pH is typical for DES containing organic acids, which dissociate in the DES matrix to release protons, significantly lowering the pH.

The low pH is advantageous in applications where an acidic medium is required, such as in the extraction of bioactive compounds like anthocyanins from plant materials. These acidic conditions can enhance the solubility and stability of certain compounds, making ChCl+CA and ChCl+MA a promising candidate for such extraction processes.

The pH of a solvent can affect the ionization state of solutes, which in turn influences their solubility and extraction efficiency. The study by Florindo et al. discusses how the pH of DESs based on choline chloride and carboxylic acids can be tuned by varying the ratio of the components, thereby affecting the extraction of different compounds. Florindo (2014).

Water Content Measurement

The water content of the successfully synthesized DES was measured to evaluate their hygroscopic properties. The results revealed that ChCl+CA contained 7.42% water, while ChCl+MA had a slightly lower water content of 5.13%**.**

The higher water content of 7.42% observed in ChCl+CA is likely due to the polyfunctional nature of citric acid, which can form multiple hydrogen bonds with water molecules. Citric acid's three carboxyl groups create extensive networks of hydrogen bonding, which increase the DES's ability to attract and retain moisture. The slightly lower water content of 5.13% in ChCl+MA reflects the lesser extent of hydrogen bonding interactions compared to citric acid. Malic acid, with two carboxyl groups, has fewer sites for hydrogen bonding, resulting in a reduced capacity to attract water . The presence of water in DESs can enhance the solubility of certain compounds, thereby improving extraction efficiency. Bo (2015).

FTIR Analysis

The formation of the ChCl+MA DES and the interactions between the two molecules were studied using FTIR spectroscopy. The FTIR spectra of pure choline chloride, malic acid, and their eutectic mixture (ChCl+MA) were analyzed to identify the specific interactions occurring within the DES.

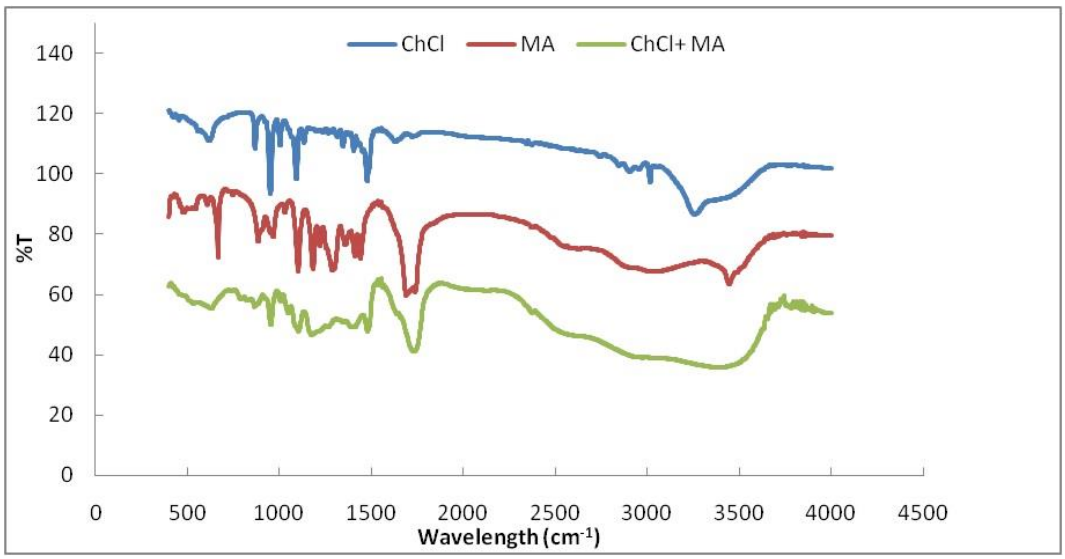

Figure 2. Choline Chloride and Malic Acid (ChCl+MA) DES IR Spectrum

Figure 2 shows the FTIR spectra of pure choline chloride, malic acid, and the ChCl+MA deep eutectic solvent (DES). In the ChCl spectrum, a broad band at 3257.77 cm^{-1} is attributed to O-H stretching, indicating hydrogen bonding in the choline chloride structure. Additional bands at 3016.67 cm^{-1} correspond to C-H stretching from the methyl groups, while peaks at 1477.47 cm^{-1} and 1404.18 cm^{-1} are associated with alkyl group deformation. The C-N stretching of the quaternary ammonium group is observed at 1091.71 cm^{-1}, characteristic of choline chloride. The

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malic acid spectrum shows a strong absorption peak at 1737.86 cm^{-1}, corresponding to C=O stretching of the carboxyl group, and another at 1440.83 cm^{-1} for O-H bending. The 1300-1200 cm^{-1} range is attributed to C-O stretching vibrations in the hydroxyl and carboxyl groups of malic acid.

The FTIR spectrum of ChCl+MA DES reveals key shifts indicating the formation of the eutectic mixture. The O-H stretching band from ChCl, initially at 3257.77 cm^{-1}, shifts to 3387.00 cm^{-1} in the DES, confirming strong hydrogen bonding between malic acid's hydroxyl and carboxyl groups and choline chloride's chloride ion (Dai, 2013). The C=O stretching vibration, which appears at 1737.86 cm^{-1} in pure malic acid, shifts to 1728.22 cm^{-1} in the DES, suggesting interaction between the carbonyl group and chloride, weakening the bond slightly due to hydrogen bonding with the chloride ion. This shift is typical in DES systems (Dadbin, 2013). The C-H stretching at 3016.67 cm^{-1} in pure ChCl becomes less prominent in the ChCl+MA DES spectrum, indicating that the methyl groups participate in hydrogen bonding, contributing to the DES stability. Furthermore, the C-O stretching vibrations in malic acid, observed at 950.91 cm^{-1}, shift slightly to 954.76 cm^{-1} in the DES, further supporting the involvement of the hydroxyl group in hydrogen bonding with chloride ions. The broadening of bands between 1100-900 cm^{-1} confirms the extensive hydrogen bonding within the DES, as also reported in similar systems (Max, 2002).

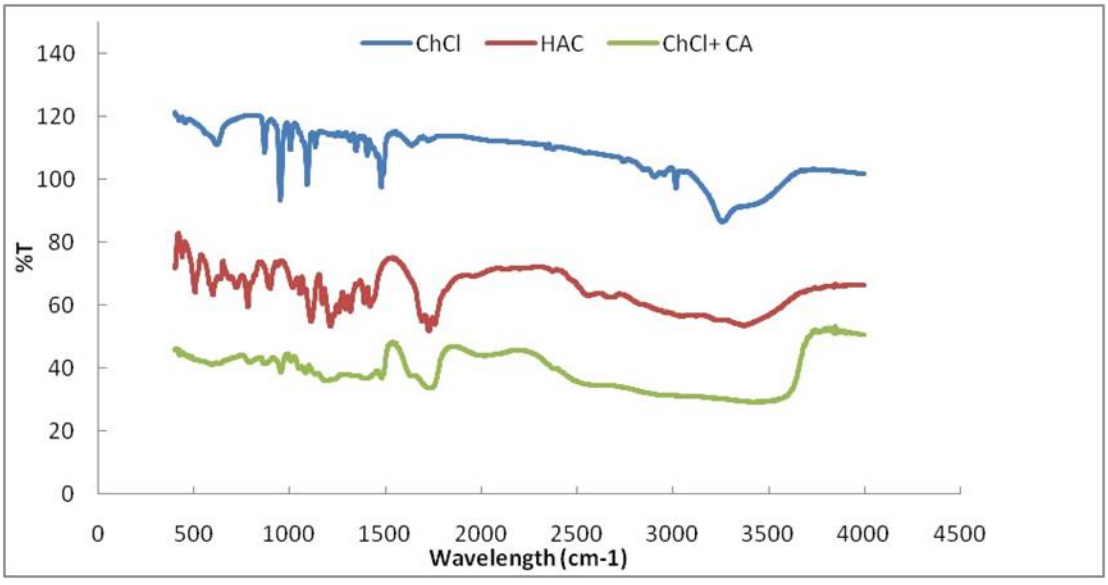

Figure 3. Choline Chloride and Citric Acid (ChCl+CA) DES IR Spectrum

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Figure 3 presents the FTIR spectra of pure choline chloride, citric acid, and the ChCl+CA deep eutectic solvent (DES). Citric acid exhibits strong absorption bands at 1757.15 cm^{-1} and 1726.29 cm^{-1}, corresponding to the C=O stretching of carboxyl groups and C–O stretching vibrations, respectively. These peaks reflect the functional groups in citric acid, which play a key role in hydrogen bonding with choline chloride. In the ChCl+CA DES spectrum, overlapping bands from both components are observed. Notably, the O-H stretching vibration shifts to 3431.36 cm^{-1}, indicating changes in hydrogen bonding due to interaction with citric acid. The C=O stretching band shifts from 1726.29 cm^{-1} in pure citric acid to 1724.36 cm^{-1} in the DES, further confirming the formation of hydrogen bonds.

The shifts in O-H and C=O stretching vibrations in the ChCl+CA DES spectrum compared to the pure components suggest successful DES formation. These shifts arise from hydrogen bond formation between the hydroxyl groups of choline chloride and the carboxyl groups of citric acid, altering the vibrational frequencies due to changes in the electronic environment (Kahar, 2011). The broadening of bands between 3200 cm^{-1} and 3600 cm^{-1} in the DES spectrum relative to pure citric acid indicates increased hydrogen bonding. This broadening reflects the more complex hydrogen bonding network in DES systems, where components interact more extensively than in their isolated forms.

CONCLUSION

The study effectively highlights the potential of Choline Chloride-based Deep Eutectic Solvents (DES) as sustainable alternatives to conventional solvents, with the successful synthesis of ChCl+CA and ChCl+MA at a 1:1 molar ratio demonstrating their strong hydrogen bonding capabilities. These findings not only underscore the versatility of DES but also point to their promising use in extraction processes, particularly for natural pigments. DES have shown significant potential in pigment extraction**,** offering advantages like low toxicity, biodegradability, and the ability to enhance the solubility of bioactive compounds. In future research, these extracted pigments, derived from natural sources, can be utilized as cosmetic pigments, aligning with the growing demand for sustainable and natural ingredients in the cosmetics industry. The customizable nature of DES allows for the selective extraction of pigments while preserving their stability and color properties, essential for cosmetic applications. The limitations identified in DES synthesis, such as viscosity and scalability, remain challenges

to be addressed, but the successful extraction of pigments using DES opens the door to new, eco-friendly cosmetic formulations. Further research will explore the optimization of DES for pigment stability, color intensity, and safety, ensuring that these natural pigments meet the regulatory and performance standards required for cosmetic use. By leveraging the green chemistry principles of DES, this work sets the stage for future developments in cosmetic pigment extraction, contributing to the broader shift towards sustainable, plant-based ingredients in the cosmetics industry.

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