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POTENTIAL GREEN LIQUID FROM TERNARY DEEP EUTECTIC SOLVENT COMPOSED OF GALLIC ACID, UREA, AND ZINC CHLORIDE: CHARACTERIZATION OF THEIR PHYSICOCHEMICAL AND THERMAL PROPERTIES

(Potensi Cecair Hijau daripada Pelarut Eutektik Terdalam Ternari daripada Asid Galik, Urea, dan Zink Klorida: Pencirian Sifat Fisikokimia dan Termanya)

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Abstract

Deep eutectic solvents (DESs) have attracted wide attention due to their cheaper cost, ease of manufacture, lower toxicity, and higher biological compatibility. In this study, we offer a more affordable and adaptable path to similar systems using gallic acid (GA), urea (U), and zinc chloride ($ZnCl_2$). The mixture produced, called GA-based DES, was prepared at varying molar ratios of 1:5:1, 1:6:1, 1:7:1, and 1:8:1 (GA:U:$ZnCl_2$). The eutectic liquid form of the GA-based DES mixture was obtained when heated at an operating temperature of 120 °C, below the melting temperature of each individual chemical. The structural and physicochemical properties of the DESs were studied via Fourier transform infrared spectroscopy, thermogravimetric analysis, and viscosity test. Different molar ratios of the DES mixture affected the hydrogen bond interaction formed between GA and U as the hydrogen bond donors and $ZnCl_2$ as the hydrogen bond acceptor in the DES mixture with the presence of O–H stretching and N–H stretching vibration bands as an association effect of GA, U, and $ZnCl_2$. An increase in the U ratio weakened the hydrogen bond and reduced the viscosity of the liquid in the DES mixture due to an increase in O–H stretching. The current findings provide a potential justification for the viscosity of DES mixtures and aid in tailoring the design and development of new DES mixtures for further applications, such as extraction, separation, conversion to functional porous carbon, and biochemical technology.

Keywords: chemical properties, deep eutectic solvent, gallic acid, urea, physical properties

Abstrak

Pelarut eutektik terdalam (DES) telah menarik perhatian luas kerana kosnya yang lebih murah, kemudahan pembuatan, ketoksikan yang lebih rendah, dan keserasian biologi yang lebih tinggi. Dalam kajian ini, kami menawarkan laluan yang lebih berpatutan dan boleh disesuaikan kepada sistem serupa menggunakan asid galik (GA), urea (U), dan zink klorida ($ZnCl_2$). DES berasaskan GA yang dihasilkan dalam kajian ini adalah daripada campuran GA-U-$ZnCl_2$ yang terdiri daripada empat nisbah molar berbeza iaitu 1:5:1, 1:6:1, 1:7:1, dan 1:8:1. Cecair eutektik campuran DES berasaskan GA diperoleh apabila dipanaskan pada suhu operasi 120 °C di bawah suhu lebur setiap bahan kimia. Sifat struktur dan fizikokimia DES dikaji melalui spektroskopi inframerah transformasi Fourier, analisis termogravimetri, dan ujian kelikatan. Nisbah molar campuran DES yang berbeza mempengaruhi interaksi ikatan

hidrogen yang terbentuk antara GA dan U sebagai penderma ikatan hidrogen dan $ZnCl_2$ sebagai penerima ikatan hidrogen dalam campuran DES dengan kehadiran regangan O–H dan jalur getaran regangan N–H sebagai kesan persatuan GA, U, dan $ZnCl_2$. Peningkatan nisbah U melemahkan ikatan hidrogen dan mengurangkan kelikatan cecair dalam campuran DES disebabkan oleh peningkatan dalam regangan O–H. Penemuan semasa memberikan justifikasi yang berpotensi untuk kelikatan hasil daripada campuran DES dan membantu dalam menyesuaikan reka bentuk dan perkembangan campuran DES baharu untuk aplikasi selanjutnya.

Kata kunci: sifat kimia, pelarut eutektik dalam, asid galik, urea, ciri-ciri fizikal

Introduction

Green chemistry stands at the forefront of scientific endeavors, focusing on creating sustainable procedures and substances. With recent industrial growth causing substantial harm to the environment, various substitutes for processes and solvents have emerged to reduce this adverse impact. Ionic liquids (ILs) were introduced as one such substitute solvent in the past few decades and have increasingly gained attention. Ionic liquids have obtained significant interest, particularly in the realms of catalysis, material chemistry, and preprocessing of biomass [1]. The creation of a liquid-phase product, known as a eutectic mixture, arises from the combination of specific precursor components during the synthesis of ILs. Nevertheless, it has been confirmed that these solvents come with specific disadvantages, such as costly synthesis, purification demands, and toxicity [2]. The claimed environmental friendliness of these modern solvents is currently a subject of considerable debate in existing literature [3]. Numerous reports have highlighted the potentially harmful toxicity and the notably low biodegradability of the majority of ILs [4, 5, 6]. Moreover, their synthesis is far from environmentally friendly, as it typically necessitates a substantial quantity of salts and solvents for complete anion exchange. These shortcomings, coupled with the elevated cost of conventional ILs, regrettably impede their industrial advancement. Consequently, there is a pressing need for innovative approaches to employ these systems in a more judicious manner [1].

Therefore, in recent years, a fresh class of so-called green solvents known as deep eutectic solvents (DESs) has emerged as a promising alternative. Deep eutectic solvents are formed by combining two or more salts, incorporating both hydrogen bond acceptors (HBAs) and hydrogen bond donors (HBDs), such as amides, amines, alcohols, and carboxylic acids [7, 8, 9], which then could be capable of engaging in hydrogen bonds and electrostatic interactions. This combination leads to the formation of a eutectic mixture [6, 10, 11]. Moreover, many HBDs and HBAs have been identified as capable of forming DESs through self-association. The distinctive solvent characteristics of DESs enable a broad spectrum of solutes to exhibit significant solubility in such solvents under certain specific conditions [12]. These properties collectively offer the potential to utilize DESs as an environmentally friendly and effective alternative to traditional methods for synthesizing functional materials. For instance, they can serve as solvent precursors and even contribute to the production of functional carbon material sources. The synthesis of DESs has gained wide attention in numerous literatures. Wang et al. [9] produced DES from different sources of HBAs and HBDs (i.e., tyrosine, urea, and zinc chloride), while Wei et al. [13] applied novelty in synthesizing DES from the mixture of boron acid, choline chloride, and urea. Besides, the key characteristic that sets DESs apart is that their melting point is notably lower than that of the individual components. In some cases, this reduction in melting point can be quite substantial, leading to a liquid mixture even at room temperature.

Furthermore, DESs embody all the favorable attributes of an environmentally friendly and relatively safe solvent [14]. This family of compounds provides numerous benefits, such as straightforward preparation with high levels of purity and yield [15]. Furthermore, DESs are also recognized for their non-toxicity, biodegradability, biocompatibility, and minimal vapor pressure [3, 16]. In addition, DESs hold significant promise in various industrial applications, including organic synthesis, extraction processes,

electrochemistry, enzymatic reactions, and the purification of biodiesel and flavonoids [17, 18, 19]. Some eutectic systems have already demonstrated their ability to dissolve complex lignocellulosic materials like lignin, hemicellulose, cellulose, and starch, yielding successful outcomes.

In this specific context, we introduce a cost-effective and adaptable approach to develop DES systems. This innovative method involves combining gallic acid (GA), urea (U), and zinc chloride ($ZnCl_2$) to create a DES. The inclusion of GA and U, along with $ZnCl_2$ salt, results in a solvent with unique properties. The presence of the amino group ($-NH_2$) in U influences the stretching of O–H bonds, thus impacting the hydrogen bond interaction between the HBD and HBA of $ZnCl_2$ salt in the DES. Luo et al. [20] reported on the synthesis of DES consisting of phenols/ketones, specifically utilizing tannic acid and U. This approach was identified as a favorable pathway for hydrogen bond interaction, with tannic acid serving as the carbon precursor and U as the nitrogen precursor. Carriazo et al. [21] also prepared DES from a phenolic compound, specifically a resorcinol-based DES acting as both a soft template and carbon source. Consequently, drawing inspiration from these previous studies, GA, which is categorized under the phenolic acid group, was chosen as a precursor in this investigation due to its natural origin, cost-effectiveness, and ready availability.

The experimental conditions, including the molar ratio of precursors, were varied to emphasize their impact on bond interaction, composition, morphology, and structural characteristics of the resulting DES. Varied molar ratios of DES mixtures influence hydrogen bond interactions among GA, U (HBD), and $ZnCl_2$ (HBA). This is evident through the O–H and N–H stretching vibration bands, representing the association effect between the individual components. The optimized sample exhibits exceptional solvent and functional performance when utilized as a solvent or other functional materials. This research aims to comprehensively characterize DES systems derived from GA, U, and $ZnCl_2$, providing insights into their physical, chemical, and thermal properties. The ultimate goal is to deepen our understanding of their potential applications, with a specific focus on producing custom porous carbon in future studies.

Materials and Methods

Preparation of des samples at different molar ratios

Chemically pure $ZnCl_2$ and silicone oil were purchased from R&M Chemicals (Selangor, Malaysia), while GA (98%) and U (99.5%) were purchased from Acros Organics (Selangor, Malaysia). The DESs were prepared using various molar ratios of GA, U, and $ZnCl_2$ mixture with GA as a carbonaceous precursor and U as a nitrogen precursor. Zinc chloride was also added as a porogen and activating agent. Figure 1 presents the raw materials used in the synthesis of the DES samples. A round-bottom flask immersed in an oil bath heated by a heating plate was used to prepare the DES mixture. The physical mixture of GA, U, and $ZnCl_2$ in a molar ratio of 1:5:1 was heated at 120 °C with steady stirring until a homogeneous liquid was formed. To investigate the influence of precursor material ratios on the hydrogen bond formation in the synthesized DESs, the molar ratios of GA to U and $ZnCl_2$, designated as Ga:U:$ZnCl_2$, were established at 1:6:1, 1:7:1, and 1:8:1. Figure 2 depicts the experimental set-up.

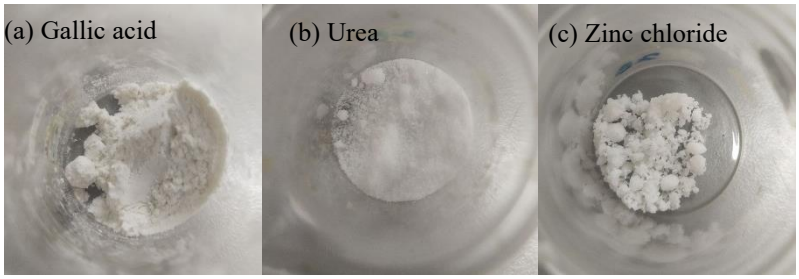

Figure 1. The raw materials of a) gallic acid, b) urea, and c) zinc chloride

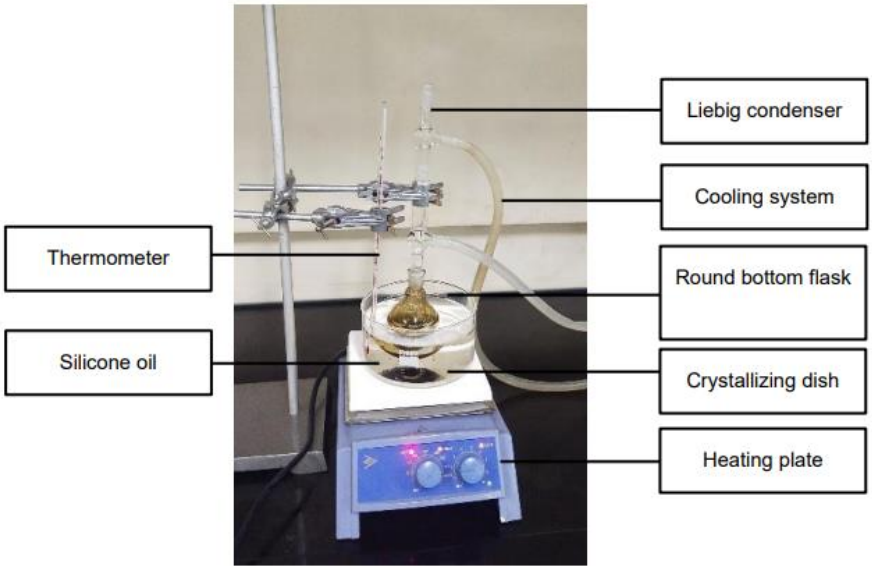

Figure 2. The experimental set-up for DES preparation

Characterization of DESs: The structural and physicochemical properties

The effect of different molar ratios of U content on the structural and physicochemical properties of GA-based DES samples was investigated in depth using viscosity test and Fourier transform infrared (FTIR) spectroscopy analysis. The viscosity test was conducted in this study using a stainless steel digital viscometer (ATAGO VISCO) for each four different molar ratios of DESs. The test was conducted under the operating temperature of 46 °C at 1.0 rpm for each run. Three measurements of the viscosity were taken for each DES sample, and the average values and standard deviations are shown as results. Besides, studies on the chemical structure and functional groups present in the GA-based DES samples produced from four different molar ratios were conducted via FTIR spectroscopy analysis. The wavenumber scans of the FTIR were adjusted to the range 4000–500 cm^{-1}.

Results and Discussion

Physical properties of DESs

To explore the optimal parameters for the formation of DESs, various molar ratios of GA, U, and $ZnCl_2$ were examined. The criteria for assessment included the time required for DES formation, the highest temperature reached during the process, the appearance of the mixture during heating, and the emergence of a homogeneous liquid state. Table 1, Figure 3, and Figure 4 present some physical characteristics of DES mixtures at different molar ratios when subjected to heating in an oil bath.

The evolution of DES formation at the tested ratios was monitored over a 20-min duration at a temperature of 120 °C. Based on visual observations, DESs at various ratios exhibited the formation of highly viscous and adhesive dark brownish liquids, with no apparent color differences among them. However, it was noted that the viscosity of the samples varied, with DES-1:8:1 being the least viscous among the investigated ratios. To validate this finding, viscosity analysis was conducted.

The physical properties of the GA-U- $ZnCl_2$ DES mixtures were determined via the viscosity test for each sample at different molar ratios of DESs using a digital viscometer set at 1.0 rpm. Table *2* presents the data obtained from the viscosity test at different molar ratios of Ga:U:$ZnCl_2$.

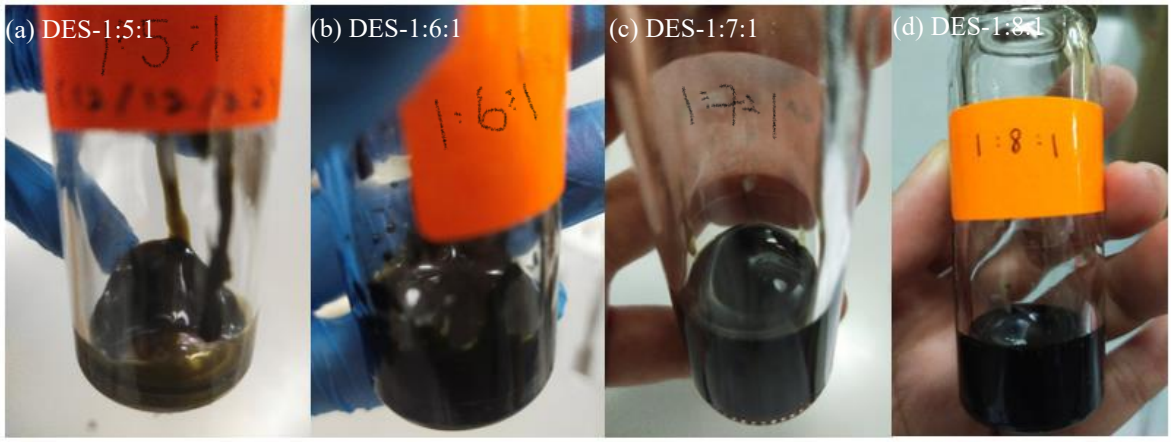

Figure 3. Visual observation of the DES samples at different ratios: a) DES-1:5:1, b) DES-1:6:1, c) DES-1:7:1, and d) DES-1:8:1

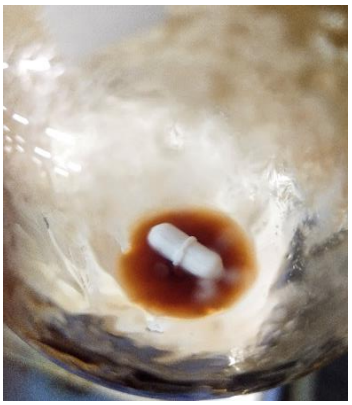

Figure 4. The initial appearance of the DES mixture which turned into a homogeneous brown liquid during heating

Table 1. Properties of DES formation at different molar ratios

Molar Ratio (GA:U:$ZnCl_2$)	**Time (min)**	**Temperature (˚C)**	**Appearance during Heating**	**Appearance at Room Temperature**
1:5:1	15	120	Melts into a brown liquid	Highly viscous mixture with a sticky texture
1:6:1	15	120	Melts into a brown liquid	Highly viscous mixture with a sticky texture
1:7:1	15	120	Melts into a brown liquid	Highly viscous mixture with a sticky texture
1:8:1	15	120	Melts into a brown liquid	Highly viscous brownish liquid with a sticky texture

Table 2. Viscosity of DESs at different molar ratios

Molar Ratio of Ga:U:$ZnCl_2$	**Viscosity Reading (cP)**			
	1st	2nd	3rd	Average
1:5:1	1,400.80	1,399.50	1,400.50	1,400.50 ± 0.89
1:6:1	1,363.60	1,363.20	1,362.10	1,362.97 ± 0.78
1:7:1	1,317.70	1,315.70	1,316.20	1,316.53 ± 1.04
1:8:1	1,063.40	1,062.80	1,063.37	1,063.37 ± 0.55

The interactions between DES components and their macroscopic properties are well-recognized to be strongly connected. Determining the physical characteristics of the DES would therefore be greatly influenced by the hydrogen bond interactions [22] and this statement is aligned with other researchers, in which the hydrogen bonding, van der Waals force, and electrostatic force interaction are the main factors that viscosity is highly dependent on [23, 24, 25]. Viscosity is considered to establish a link between the potency of hydrogen bonds in DESs and their viscosities, which denotes the intrinsic resistance to flow and reflects the intensity of intramolecular interactions within the liquid. *Table 2* illustrates that an increase in the molar ratio, indicating a higher U content in the DESs, results in a decrease in viscosity readings. The sequence of DES-1:5:1 > DES-1:6:1 > DES-1:7:1 > DES-1:8:1 corresponds to a decrease in viscosity.

In this system, U and GA functioned as HBDs, while $ZnCl_2$ acted as a HBA. Increasing the HBD content in the DESs resulted in a reduction in viscosity, primarily due to a decrease in hydrogen bond interactions formed between the chloride ion of salt as HBA and HBD components in the DES mixture. This finding aligns with the results reported by Ghaedi et al. [7], where they observed a similar trend of decreasing viscosity with an increasing amount of HBDs. As the HBD content increases, the hydrogen bonding between the HBD and HBA weakens, which results in an increase in OH stretching bonds, ultimately resulting in lower viscosity [7]. According to Yang et al. [26], one of the major challenges in producing DESs is their typically high viscosity, which can limit mass transfer when used as a solvent. For practical solvent applications, achieving low viscosity in DESs is desirable to enhance mass transfer [7, 27, 28]. Therefore, based on the viscosity test results presented in *Table 2*, DES-1:8:1 can be considered the optimal molar ratio when compared to the other three molar ratios (DES-1:5:1, DES-1:6:1, and DES-1:7:1) because it exhibits the lowest viscosity. Figure 5 depicts the structural elements of GA, U, and $ZnCl_2$ in the synthesis of DES. The precursor components exhibit hydrogen bonding resulting from the interaction between the HBA and HBD.

Chemical properties of DESs

In this study, we formulated and examined newly developed natural DESs. It is common knowledge that DESs comprise HBDs and HBAs. These blends were prepared using a naturally occurring aromatic organic acid, GA, and U as the HBDs, with $ZnCl_2$ as the HBA, and their corresponding spectra are shown in Figure 6a -Figure *6*c. Figure 6d also displays the FTIR spectra of DESs with varying compositions. In accordance with the research by Pena-Solorzano et al. [29], the presence of vibrational bands associated with the NH_2 group is denoted by a peak falling within the range of 3500–3200 cm^{-1}. The peaks located at 1623 and 1461 cm^{-1}, as depicted in Figure 6a, can be attributed to the NH and C-N bending characteristics observed in the pure U sample. Furthermore, a C=O stretching peak is evident at a wavenumber of 1678 cm^{-1}, which aligns with the findings reported by other researchers [30]. Regarding the standard GA depicted in Figure 6b, the spectral region spanning from 3600 to 2500 cm^{-1} is associated with the stretching vibrations of the OH group, and a distinct and sharp OH band is noticeable at 3471 cm^{-1}. Furthermore, the presence of a carbonyl group is indicated by a robust and narrow peak at 1635 cm^{-1}. In addition, the bands appearing at 1635, 1535, and 1431 cm^{-1} are characteristic of stretching vibrations within the C–C bonds present in the aromatic ring of GA. These frequencies closely resemble those previously reported in the literature [31]. Additionally, several other peaks observed in the range of 136–1030 cm^{-1} can be attributed to stretching vibrations associated with the C–O bonds and the bending vibration of the O–H bond within GA. In contrast, the spectra for $ZnCl_2$ (Figure 6c) reveal a vibrational band at 3519 cm^{-1}, which is characteristic of the O–H stretching bond. Furthermore, the spectrum at a wavenumber of 1605 cm^{-1} indicates the presence of O–H bending vibrations in the pure $ZnCl_2$ sample. According to the findings of Pena-Solorzano et al. [29], the occurrence of the O–H bond can be attributed to the presence of water molecules, potentially resulting from the retention of moisture in the sample during analysis. Zinc chloride is known to be hygroscopic, meaning it tends to form hydrates when exposed to water molecules.

Subsequently, FTIR analyses were conducted on various DES samples at different molar ratios, as illustrated in Figure 6d. In general, it can be observed that the four different molar ratios of DESs exhibit minimal variation in the detected peaks and possess relatively similar spectral patterns. The strong C=O band appears distinctly at 1620 cm^{-1} (narrow) and exhibits peaks at 3435 cm^{-1} (broad) in the characteristic bands of DES samples, which can be attributed to the interactions between hydrogen bonds involving the HBD urea, as well as the presence of water content. The stretching vibrations of the C–O bond at 1030 cm^{-1} suggest that the structure of GA remains largely intact within the DES system, demonstrating that the fundamental structural characteristics of GA are preserved in the DESs. When comparing the spectra of pure U (Figure 6a) with the DES samples, a shift in the carbonyl vibration of U is evident, moving from 1678 cm^{-1} to peak wavenumbers at 1573.30, 1573.79, 1572.99, and 1573.11 cm^{-1} for the DES mixtures in Figure 6d. These shifts can be attributed to the formation of coordination bonds primarily between the metal ion and the oxygen atom within the carbonyl group of U [32]. Additionally, Mariappan et al. [30] suggested that these peaks are associated with the C=O stretching vibrations present in the DES samples. Furthermore, the peaks at 1452.06, 1450.34, 1445.35, and 1447.24 cm^{-1} for DES ratios of 1:5:1, 1:6:1, 1:7:1, and 1:8:1 indicate C-N bending attributed to U, as reported.

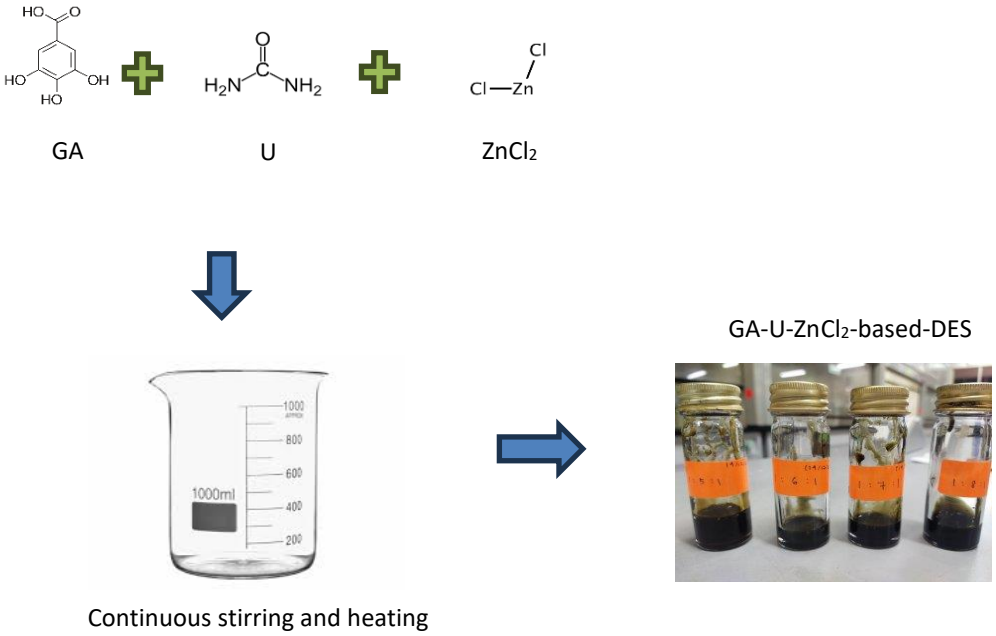

Figure 5. Structural formation of DES from precursor components

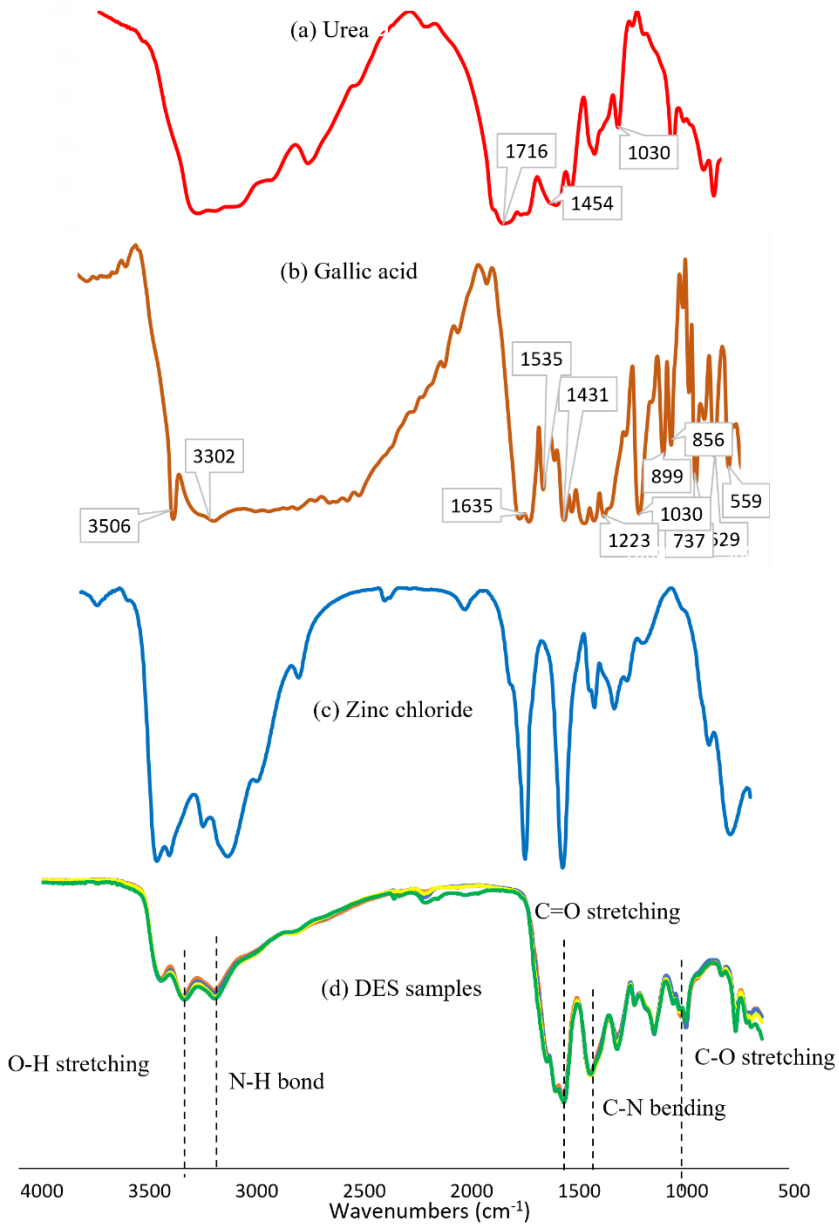

Figure 6. FTIR spectra of DES samples

Thermal properties of DESs

In most cases, hydrogen bond interactions between HBD and HBA result in the formation of homogeneous DES mixture [33]. Hence, the thermal stability of DES was evaluated via thermogravimetric analysis (TGA). Throughout this analysis, the decomposition of HBD and HBA in the investigation at different molar ratios can be determined and studied. According to Chen et. al. [33], at high temperatures, DESs often initially break down into HBDs and HBAs due to the weakening of the hydrogen bond interactions. The volatilization or decomposition of HBA with relatively low boiling points or weak stabilities occurs at a lower temperature than that at which the corresponding HBD occurs [34].

The thermal behavior study of the neat components used in the production of DES is illustrated in thermogravimetric (TG) and differential

thermogravimetric (DTG) thermograms shown in Figure 7. Urea has the lowest boiling point in comparison to GA and $ZnCl_2$. Thus, from Figure 7a, U starts to decompose at an early temperature of 154 °C. Additionally, U shows no further decomposition after 650 °C, which is earlier than the temperatures at which GA (839 °C) and $ZnCl_2$ (723 °C) no longer exhibit decreases in sample weight. The findings from the experiments are aligned with Chen et. al [33], who stated that an HBA generally has poor thermal stability and low boiling temperature, which can cause them to break down or volatilize early during TGA analysis, where U is the HBA in the preparation of the DES sample.

From Figure 7a, the TGA curves demonstrate the first step of weight loss at 86 °C, which might be due to the elimination of crystalline water [35]. The DTG curves show the onset of weight loss at 264 and 320 °C. On the other hand, the initial stage of weight percentage loss for U (Figure 7b) is at 154 °C. The TG thermogram of $ZnCl_2$ shows two steps of the thermal degradation process, where the material had lost around 1.025% and 85.72% in the first and second steps of degradation, respectively, of their total original weight during this process (Figure 7c). The pattern of thermal degradation of $ZnCl_2$ was nearly identical to one of the reported data [35]. The thermogram of the sample disclosed the temperature of the maximum derivative weight loss (T_{max}) at 570 °C. This TG/DTG thermal characteristic information would be helpful for the preparation of eutectic systems.

The thermal stability of DES mixtures can be investigated through TGA and DTG thermal decomposition profiles, which are presented in Figure 8. The TGA and DTG curves extend over the temperature interval (25–900 °C) within which the TGA was conducted. From Figure 8, it can be seen that an initial mass loss (stage A) occurred between the temperature of 25 °C and 110 °C for all samples due to moisture loss. Another peak (stage B) exists in a range of 110–280 °C, which corresponds to the decomposition of U [23]. The mass loss in stage C (from 280 to 400 °C), on the other hand, is due to the decomposition attributed to polymer formation (e.g., monoester and diester) due to the complex reaction among chloride, GA, and U [36]. The onset temperature of sample thermal degradation (T_{onset}), usually defined by 10% mass loss curve, is also a relevant parameter to be investigated through the TGA-DTG thermograms [36]. This temperature establishes the temperature range at which the samples can be utilized without degrading. The values of T_{onset} for DES-1:5:1, 1:6:1, 1:7:1, and 1:8:1 are 180, 181, 176.8, and 175 °C, respectively. These results portray an enhanced thermostability of HBD, particularly U, which initially has a low T_{onset} (154 °C). From the thermal stability point of view between the DES mixture prepared at different molar ratios, $ZnCl_2$ is more heat stable than U; hence, the T_{onset} of DES mixture would decrease with the increased ratio of U. This phenomenon can be ascribed to the surplus U present in the mixture prior to the formation of DES with $ZnCl_2$ (HBA). Overall, the composition appears to resemble a combination of DES and impurities (excess U), indicating that it is not an entirely DES-based system despite the formation of certain hydrogen bonds and the preparation of an approximate eutectic mixture. Additionally, from the TGA and DTG curves, when the U concentration increased, the maximum decomposition temperature (T_{peak}) shifted to higher temperatures. The coordinating nature of the ions, intermolecular interaction, and excess U might explain the rise in thermal decomposition temperatures [27]. These results show that the change in molar ratio has a significant impact on the thermal stability of ternary DES.

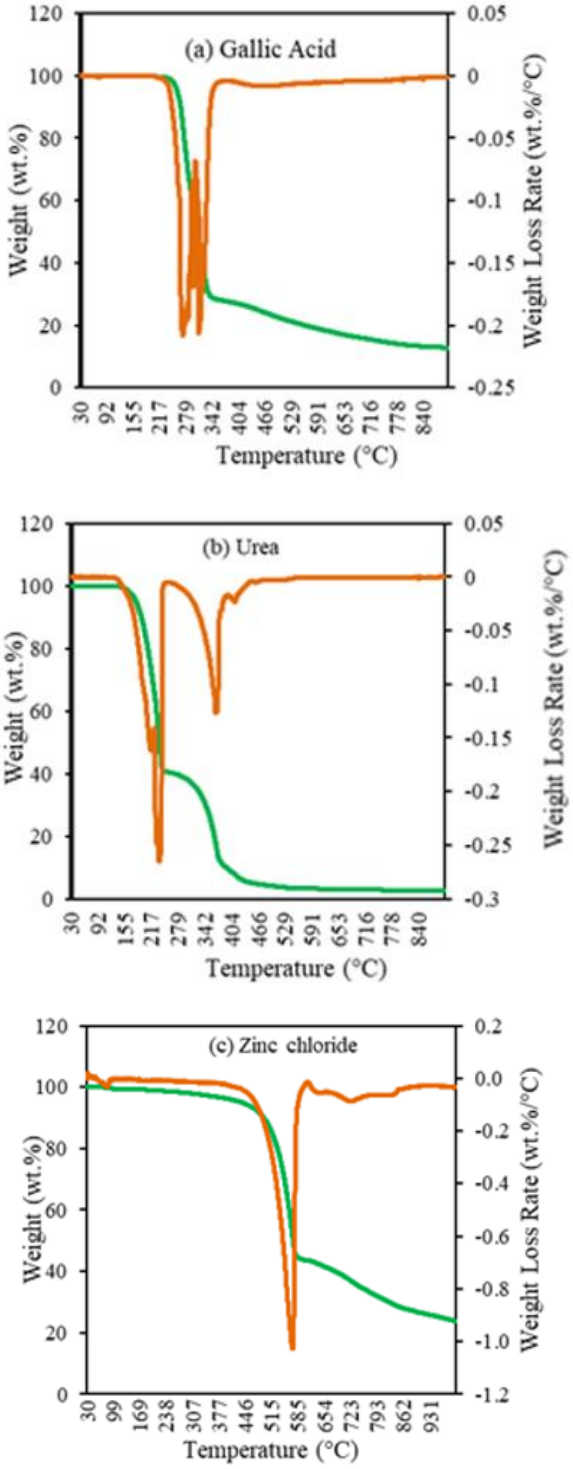

Figure 7. TGA-DTG of the components in DES

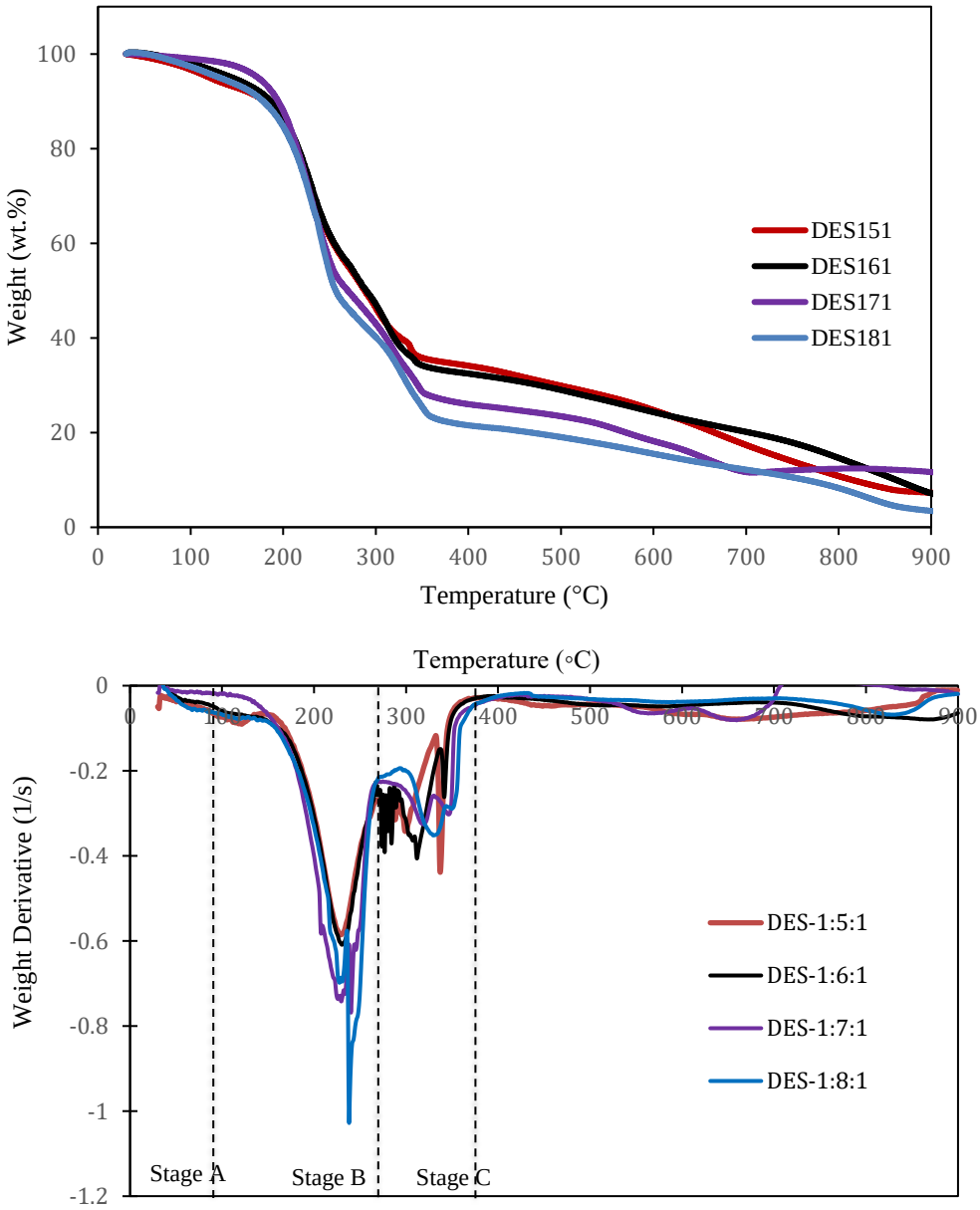

Figure 8. TGA-DTG of the DES samples

Conclusions

In this investigation, a series of DESs was successfully produced using natural components, including GA and U as HBDs, and $ZnCl_2$ as both the salt and HBA. Four different molar ratios, denoted as DES-1:5:1, DES-1:6:1, DES-1:7:1, and DES-1:8:1, were employed for the synthesis. The viscosity results indicated that DES-1:8:1 exhibited the lowest viscosity, suggesting that an increased U (HBD) content led to a reduction in viscosity due to weakened hydrogen bonding resulting from increased O–H stretching during DES synthesis. Furthermore, the FTIR analysis revealed that the GA structure predominantly maintained its integrity within the DES system, as evidenced by the C–O stretching. Additionally, the TGA showed that the thermal stability depended on the molar ratio for the ternary eutectic

mixtures. By carefully choosing an appropriate molar proportion of HBDs and HBAs, particularly focusing on the HBDs, it becomes feasible to synthesize DESs possessing the desired level of thermal stability. This study introduces a novel approach to synthesizing environmentally friendly ternary DESs, showcasing noteworthy properties that hold promise for applications in functional solvents and other materials. The findings not only contribute to advancing the formulation of novel ternary natural DESs but also offer insights for future applications and the customization of formulations in this field.

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References

1. Zhang, Q., Vigier, K. D. O. and Jerome, F. (2012). Deep eutectic solvents: syntheses, properties and applications. *Chemistry Society Review*, 41: 7108-7146.
2. Hikmawanti, N. P. E., Ramadon, D., Jantan, I. and Mun'im, A. (2021). Natural deep eutectic solvents (Nades): Phytochemical extraction performance enhancer for pharmaceutical and nutraceutical product development. *Plants*, 10(10): 2091.
3. Chandran, K., Kait, C. F., Wilfred, C. D. and Zaid, H. F. M. (2021). A review on deep eutectic solvents: Physiochemical properties and its application as an absorbent for sulfur dioxide. *Journal of Molecular Liquids*, 338: 117021.
4. Smith, E. L., Abbott, A. P. and Ryder, K. S. (2014). Deep eutectic solvents (DESs) and their applications. *Chemical Reviews*, 114(21): 11060-11082.
5. Sekharan, T. R., Chandira, R. M., Tamilvanan, S., Rajesh, S. C. and Venkateswarlu, B. S. (2022). Deep eutectic solvents as an alternate to other harmful solvents. *Biointerface Research in Applied Chemistry*, 12(1): 847-860.
6. El Achkar, T., Greige-Gerges, H. and Fourmentin, S. (2021). Basics and properties of deep eutectic solvents: a review. In *Environmental Chemistry Letters*, 19(4): 3397-3408.
7. Ghaedi, H., Ayoub, M., Sufian, S., Shariff, A. M. and Lal, B. (2017). The study on temperature dependence of viscosity and surface tension of several Phosphonium-based deep eutectic solvents. *Journal of Molecular Liquids*, 241: 500-510.
8. Chen, L., Deng, J., Song, Y., Hong, S. and Lian, H. (2020). Deep eutectic solvent promoted tunable synthesis of nitrogen-doped nanoporous carbons from enzymatic hydrolysis lignin for supercapacitors. *Materials Research Bulletin*, 123: 110708.
9. Wang, T., Guo, J., Guo, Y., Feng, J. and Wu, D. (2021). Nitrogen-doped carbon derived from deep eutectic solvent as a high-performance supercapacitor. *ACS Applied Energy Materials*, 4(3): 2190-2200.
10. Hansen, B. B., Spittle, S., Chen, B., Poe, D., Zhang, Y., Klein, J. M., Horton, A., Adhikari, L., Zelovich, T., Doherty, B. W., Gurkan, B., Maginn, E. J., Ragauskas, A., Dadmun, M., Zawodzinski, T. A., Baker, G. A., Tuckerman, M. E., Savinell, R. F. and Sangoro, J. R. (2021). Deep Eutectic Solvents: A Review of Fundamentals and Applications. *Chemical Reviews*, 121(3): 1232-1285.
11. Wang, B., Cheng, J., Wang, D. D., Li, X., Meng, Q., Zhang, Z., An, J., Liu, X. and Li, M. (2020). Study on the desulfurization and regeneration performance of functional deep eutectic solvents. *ACS Omega*, *5*(25): 15353-15361.
12. Ge, X., Gu, C., Wang, X. and Tu, J. (2017). Deep eutectic solvents (DESs)-derived advanced functional materials for energy and environmental applications: Challenges, opportunities, and future vision. *Journal of Materials Chemistry A*, *5*(18): 8209-8229.
13. Wei, Y., Wu, P., Luo, J., Dai, L., Li, H., Zhang, M., Chen, L., Wang, L., Zhu, W. and Li, H. (2020). Synthesis of hierarchical porous BCN using ternary deep eutectic solvent as precursor and template for

aerobic oxidative desulfurization. *Microporous and Mesoporous Materials*, 293: 109788.

14. Chemat, F., Abert-Vian, M., Fabiano-Tixier, A. S., Strube, J., Uhlenbrock, L., Gunjevic, V. and Cravotto, G. (2019). Green extraction of natural products. Origins, current status, and future challenges. *TrAC Trends in Analytical Chemistry*, 118: 248-263.
15. Singh, S. (2018). Applications of green solvents in extraction of phytochemicals from medicinal plants: A review Promila and Sushila Singh. *The Pharma Innovation Journal*, *7*(3): 238-245.
16. Zainal-Abidin, M. H., Hayyan, M., Hayyan, A. and Jayakumar, N. S. (2017). New horizons in the extraction of bioactive compounds using deep eutectic solvents: A review. *Analytica Chimica Acta*, *979*: 1-23.
17. Ali, M. C., Yang, Q., Fine, A. A., Jin, W., Zhang, Z., Xing, H. and Ren, Q. (2015). Efficient removal of both basic and non-basic nitrogen compounds from fuels by deep eutectic solvents. *Green Chemistry*, 18(1): 157-164.
18. Li, Y., Ali, M. C., Yang, Q., Zhang, Z., Bao, Z., Su, B., Xing, H. and Ren, Q. (2017). Hybrid deep eutectic solvents with flexible hydrogen-bonded supramolecular networks for highly efficient uptake of NH_3. *ChemSusChem*, 10(17): 3368-3377.
19. Chemat, F., Anjum, H., Shariff, A. M., Kumar, P. and Murugesan, T. (2016). Thermal and physical properties of (Choline chloride + urea + l-arginine) deep eutectic solvents. *Journal of Molecular Liquids*, 218: 301-308.
20. Luo, R., Liu, C., Li, J., Wang, C., Sun, X., Shen, J., Han, W. and Wang, L. (2017). Deep-eutectic solvents derived nitrogen-doped graphitic carbon as a superior electrocatalyst for oxygen reduction. *ACS Applied Materials and Interfaces*, 9(38): 32737-32744.
21. Carriazo, D., Gutiérrez, M. C., Ferrer, M. L. and Del Monte, F. (2010). Resorcinol-based deep eutectic solvents as both carbonaceous precursors and templating agents in the synthesis of hierarchical porous carbon monoliths. *Chemistry of Materials*, 22(22): 6146-6152.
22. Li, C., Wang, Y., Xiao, N., Li, H., Ji, Y., Guo, Z., Liu, C. and Qiu, J. (2019). Nitrogen-doped porous carbon from coal for high efficiency CO_2 electrocatalytic reduction. *Carbon*, 151: 46-52.
23. Gutiérrez, M. C., Carriazo, D., Tamayo, A., Jiménez, R., Picõ, F., Rojo, J. M., Ferrer, M. L. and Del Monte, F. (2011). Deep-eutectic-solvent-assisted synthesis of hierarchical carbon electrodes exhibiting capacitance retention at high current densities. *Chemistry - A European Journal*, 17(38): 10533-10537.
24. Haghbakhsh, R., Parvaneh, K., Raeissi, S. and Shariati, A. (2018). A general viscosity model for deep eutectic solvents: The free volume theory coupled with association equations of state. *Fluid Phase Equilibria*, 470: 193-202.
25. Manurung, R., Simanjuntak, G. C., Perez, R. N., Syahputra, A., Alhamdi, M. A., Siregar, H. and Syahputri Zuhri, R. R. (2019). Production of choline chloride-based deep eutectic solvent with hydrogen bond donor d-glucose and ethylene glycol. *IOP Conference Series: Materials Science and Engineering*, 505(1): 012134.
26. Liu, Y., Friesen, J. B., McAlpine, J. B., Lankin, D. C., Chen, S.-N. and Pauli, G. F. (2018). Natural deep eutectic solvents: Properties, applications, and perspectives. *Journal of Natural Products*, 81(3): 679-690.
27. Savi, L. K., Dias, M. C. G. C., Carpine, D., Waszczynskyj, N., Ribani, R. H. and Haminiuk, C. W. I. (2019). Natural deep eutectic solvents (NADES) based on citric acid and sucrose as a potential green technology: a comprehensive study of water inclusion and its effect on thermal, physical and rheological properties. *International Journal of Food Science and Technology*, 54(3): 898-907.
28. Tan, P., Xue, D. M., Zhu, J., Jiang, Y., He, Q. X., Hou, Z. F., Liu, X. Q. and Sun, L. B. (2018). Hierarchical N-doped carbons from designed N-rich polymer: Adsorbents with a record-high capacity for desulfurization. *AIChE Journal*, 64(11): 3786-3793.
29. Penã-Solórzano, D., Kouznetsov, V. V. and Ochoa-Puentes, C. (2020). Physicochemical properties of a urea/zinc chloride eutectic mixture and its improved effect on the fast and high yield synthesis of

indeno[2,1-: C] quinolines. *New Journal of Chemistry*, *44*(19): 7987-7997.

30. Mariappan, M., Madhurambal, G., Ravindran, B. and Mojumdar, S. C. (2011). Thermal, FTIR and microhardness studies of bisthiourea-urea single crystal. *Journal of Thermal Analysis and Calorimetry*, 104(3): 915-921.
31. Sun, Z., Chen, Y., Ke, Q., Yang, Y. and Yuan, J. (2002). Photocatalytic degradation of a cationic azo dye by TiO_2/bentonite nanocomposite. *Journal of Photochemistry and Photobiology A: Chemistry*, 149(1): 169-174.
32. Xu, L., Guo, L., Hu, G., Chen, J., Hu, X., Wang, S., Dai, W. and Fan, M. (2015). Nitrogen-doped porous carbon spheres derived from d-glucose as highly-efficient CO_2 sorbents. *RSC Advances*, *5*(48): 37964-37969.
33. Chen, W., Xue, Z., Wang, J., Jiang, J., Zhao, X. and Mu, T. (2018). Investigation on the thermal stability of deep eutectic solvents. *Wuli Huaxue Xuebao/Acta Physico - Chimica Sinica*, 34(8): 904-911.
34. Jurić, T., Uka, D., Holló, B. B., Jović, B., Kordić, B. and Popović, B. M. (2021). Comprehensive physicochemical evaluation of choline chloride-based natural deep eutectic solvents. *Journal of Molecular Liquids*, 343: 116968.
35. González-Rivera, J., Husanu, E., Mero, A., Ferrari, C., Duce, C., Tinè, M. R., D'Andrea, F., Pomelli, C. S., and Guazzelli, L. (2020). Insights into microwave heating response and thermal decomposition behavior of deep eutectic solvents. *Journal of Molecular Liquids*, 300: 112357.
36. Kadhom, M. A., Abdullah, G. H. and Al-Bayati, N. (2017). Studying two series of ternary deep eutectic solvents (choline chloride–urea–glycerol) and (choline chloride–malic acid–glycerol), synthesis and characterizations. *Arabian Journal for Science and Engineering*, 42(4): 1579-1589.