ALCOHOL-DILUTED DEEP EUTACTIC SOLVENT AS THE ELECTROLYTE

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Abstract: Deep eutectic solvents (DESs) are promising alternatives to traditional electrolytes in electrochemical devices because of their favorable properties, including low volatility, biodegradability, and ease of preparation. This study aimed to optimize a DES composed of choline chloride and urea by investigating the effects of molar ratios and short-chain alcohol additions on viscosity, ionic conductivity, and electrochemical stability. The DES was prepared at 80°C at four molar ratios of choline chloride to urea (1:1, 1:2, 1:3, and 1:4), with a 1:2 ratio optimal for achieving a stable, homogeneous solution. Short-chain alcohols (methanol, ethanol, 1-propanol, and 1-butanol) were added to reduce viscosity and enhance conductivity. The addition of methanol and ethanol effectively lowered the viscosity and increased the ionic conductivity because of their ability to integrate into the DES matrix and disrupt hydrogen bonding. Electrochemical analysis confirmed that the oxidative stability of DESs remained unaffected by these alcohol additions, with oxidation onset consistently at approximately 1 V. These findings demonstrate that methanol and ethanol are suitable additives for improving the performance of DESs as electrolytes in electrochemical applications, enhancing both their conductivity and stability.

Keywords: deep eutactic solvent; electrolyte; alcohols; green chemistry

Abstrak: Penelitian ini mengeksplorasi sintesis dan karakterisasi deep eutectic solvents (DES) yang dibentuk dengan mencampurkan kolin klorida dengan urea pada berbagai rasio molar. Dampak penambahan alkohol rantai pendek—metanol, etanol, 1-propanol, dan 1-butanol—terhadap viskositas dan konduktivitas ionik DES diselidiki secara sistematis. Hasil penelitian menunjukkan bahwa metanol dan etanol secara efektif mengurangi viskositas DES dengan mengganggu jaringan ikatan hidrogen, sementara 1-propanol dan 1-butanol meningkatkan viskositas karena ketidakmampuan mereka untuk berintegrasi dengan baik ke dalam matriks DES. Selain itu, penambahan alkohol meningkatkan konduktivitas ionik, dengan efek yang lebih signifikan diamati pada konsentrasi alkohol yang lebih tinggi. Metanol dan etanol, dengan rantai karbon yang lebih pendek, menunjukkan peningkatan konduktivitas ionik yang lebih besar dibandingkan dengan alkohol rantai panjang. Temuan ini menunjukkan bahwa pemilihan jenis dan konsentrasi alkohol sangat penting untuk menyesuaikan sifat-sifat DES untuk aplikasi tertentu, terutama dalam sistem elektrokimia.

Kata kunci: pelarut eutektik dalam; elektrolit; alkohol; kimia hijau

INTRODUCTION

Selecting the appropriate electrolyte is crucial for electrochemical devices, such as supercapacitors, as it determines their potential range (Horn et al., 2019). Electrolytes can be categorized into aqueous-based, organic-based, and ionic liquid-based electrolytes. Aqueous electrolytes are the most commonly used but have a narrow potential range limited by water electrolysis (Zhao & Zheng, 2015). Organic-based electrolytes offer a broader potential range of 2.5–3.0 V but are flammable, posing greater safety risks (Biswas & Chowdhury, 2023). Ionic liquids overcome these limitations with wide potential ranges up to 3 V and high boiling points (He et al., 2019; Miao et al., 2021). However, their application is constrained by high costs and complex synthesis methods.

Deep eutectic solvents (DESs) have recently gained attention as promising alternatives to conventional electrolytes because of their favorable properties. These eutectic mixtures, composed of a Lewis acid (such as quaternary ammonium salts) and a hydrogen bond donor (e.g., urea or glycerol), form ionic solutions that remain liquid at room temperature (Smith et al., 2014). DESs share similarities with ionic liquids, such as low vapor pressure and nonvolatility, but they offer advantages such as ease of preparation, biodegradability, and lower costs (Florindo et al., 2019). First developed by Abbot et al. (2003) from a mixture of choline chloride and urea, DESs have since been explored in various applications, including electrochemical systems, material synthesis, biotransformations, and gas and liquid separation (Smith et al., 2014).

Despite their potential, few studies have investigated DESs as electrolytes (Azmi et al., 2022; Puttaswamy et al., 2022; Zhong et al., 2020). DESs, such as those formed from choline chloride and urea, often suffer from high viscosity (up to 1750 mPa/s) and low ionic conductivity (1.3 mS/cm) (Lapeña et al., 2020). While adding water reduces viscosity and increases ionic conductivity, it also narrows the potential range (Azmi et al., 2022).

This study proposes to address these limitations by preparing DESs from choline chloride and urea, with short-chain alcohols added to reduce viscosity. We aim to optimize DESs with low viscosity, high ionic conductivity, and a wide potential range and identify the optimal formulation for use as electrolytes in electrochemical devices.

METHOD

Materials

Choline chloride (ChCl) was obtained from Sigma–Aldrich, China. Urea was purchased from Smart Lab, Indonesia. Methanol, ethanol, propanol, and butanol were purchased from Merck Millipore, Germany. All the reagents were used as received.

Synthesis of DES

The synthesis of DES was carried out by mixing choline chloride and urea according to previous publications (Azmi et al., 2022). Choline chloride was mixed with urea at molar ratios of 1:0.5, 1:1, 1:2, 1:3, and 1:4. The mixture was stirred and heated at 80°C until a homogeneous, colorless solution formed. Several types of short-chain alcohols (methanol, ethanol, propanol, and butanol) were added to the mixture at concentrations ranging from 1 to 5%. The resulting mixtures were further characterized.

Characterization of DESs

The prepared DES was characterized via viscosity tests, ion conductivity tests, and electrochemical characterization. The viscosity was measured using an Oswald viscometer, as described in previous literature (Regina et al., 2019). The electrochemical properties were analyzed using an Autolab potentiostat. Cyclic voltammetry was conducted over a potential range of 0 V to 3 V at a scan rate of 0.01 V/min. The ion conductivity was determined via a digital conductivity meter (Thermo Scientific Expert CTS Pocket Tester; Eutech, Thermo Fisher Scientific, USA)

RESULTS AND DISCUSSION

Effect of the Molar Ratio on DES Synthesis

DES was synthesized by mixing choline chloride and urea at a temperature of 80°C at four different molar ratios: 1:1, 1:2, 1:3, and 1:4. Ratios of 1:3 and 1:4 resulted in incomplete dissolution of the urea, with visible solid urea remaining in the mixture. This observation aligns with reports in the literature suggesting that at higher urea concentrations, excess urea does not contribute to further hydrogen bonding, leading to solubility limitations (Abbott et al., 2003; Celebi et al., 2021).

Figure 1. DES solution at a Cholin Chloride-Urea ratio of 1:2

In contrast, the 1:1 and 1:2 molar ratios produced transparent and homogeneous solutions (Fig. 1). The 1:2 molar ratio, in particular, corresponds well with literature findings, where it is identified as the eutectic composition that provides optimal interactions between the hydrogen bond donor (urea) and the acceptor (chloride ions from choline chloride) (Abbott et al., 2003; Hammond et al., 2016). This specific ratio results in a stable liquid system at room temperature, supporting the ideal hydrogen bond network essential for desirable DES properties such as low viscosity and high ionic conductivity (Hammond et al., 2016). The 1:2 molar ratio is crucial because it results in the best balance between hydrogen bond donors and acceptors, enabling stable DES formation. At this ratio, the hydrogen bond network is most effective, which results in favorable physicochemical properties such as lower viscosity and enhanced ionic conductivity, as supported by molecular structuring studies (Celebi et al., 2021; Hammond et al., 2016).

The addition of short-chain alcohols, namely, methanol, ethanol, propanol, and butanol, induced phase changes in the DES. Adding methanol and ethanol up to 10% did not alter the phase of the DES. However, the addition of more nonpolar alcohols, such as propanol and butanol, resulted in a biphasic system. These alcohols did not integrate well with the choline chloride and urea DES system.

Effect of alcohol addition on DES viscosity

Fig. 2 shows the influence of the addition of methanol, ethanol, 1-propanol, or 1-butanol on the viscosity of deep eutectic solvents (DESs). The type of alcohol significantly impacts the viscosity, with methanol and ethanol decreasing the viscosity, whereas 1-propanol and 1-butanol increasing the viscosity. This reduction in viscosity upon the addition of methanol and ethanol can be attributed to their smaller molecular size and higher polarity, allowing them to integrate effectively into the DES matrix and disrupt the intermolecular hydrogen bonding networks that contribute to the intrinsic viscosity (Dou et al., 2023). In contrast, the more nonpolar and larger 1-propanol and 1-butanol disrupt the hydrogen bonding network less effectively, leading to a biphasic system and an overall increase in viscosity. The polarity of the added alcohol is crucial in determining how it interacts with the DES system.

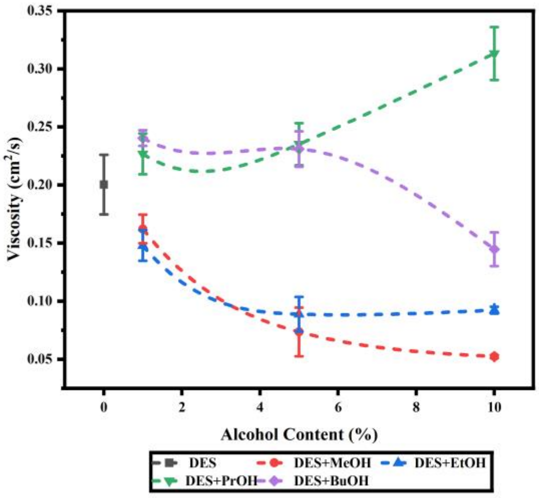

Figure 2. Viscosity of DES mixtures

Methanol and ethanol compete for hydrogen bond sites, forming new hydrogen bonds that weaken the preexisting interactions between choline chloride and urea, thus lowering the viscosity (Cotroneo-Figueroa et al., 2022). However, 1-propanol and 1-butanol are less polar and larger, leading to weaker interactions with the hydrogen bond network, which instead causes structural disruption and increases viscosity (Zhong et al., 2020).

When polar alcohols such as methanol and ethanol are introduced, their viscosity is reduced by disrupting the hydrogen bond network. These alcohols form new hydrogen bonds with both the HBD and HBA components of the DES, leading to a more disordered and less rigid structure (Cotroneo-Figueroa et al., 2022; Kumar et al., 2022). Consequently, the molecular mobility increases, resulting in a marked decrease in viscosity. Studies corroborate these findings, showing that, compared with larger, less polar alcohols such as 1-propanol and 1-butanol, smaller and more polar alcohols significantly reduce viscosity (Zhong et al., 2020).

Effect of alcohol addition on DES ionic conductivity

Figure 3 shows the effect of alcohol addition on the ionic conductivity of DES. These data indicate that alcohol introduction generally increases the ionic conductivity, primarily due to the disruption of the DES hydrogen bond network. This disruption reduces viscosity, allowing ions to move more freely, increasing their mobility and, consequently, their ionic conductivity.

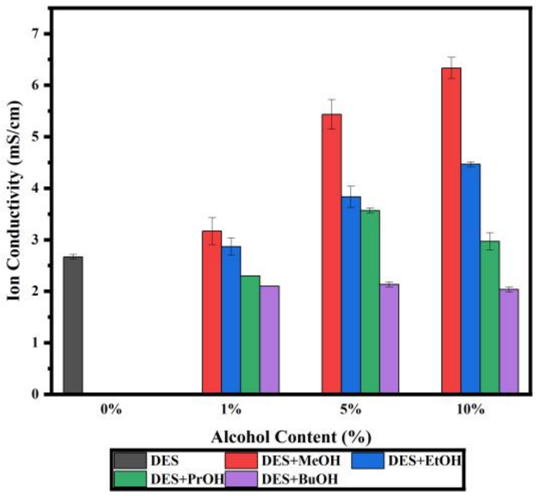

Figure 3. Ionic Conductivity of DES Mixtures

At low alcohol concentrations (e.g., 1%), the disruption of hydrogen bonding is minimal, and the corresponding increase in ionic conductivity is not significant. However, at higher concentrations (up to 10%), the disruption is more substantial, resulting in a more pronounced increase in ionic conductivity. These findings are consistent with research showing that viscosity is inversely correlated with ionic conductivity in DES systems (Azmi et al., 2022; Kumar et al., 2022).

Additionally, Fig. 3 suggests that alcohols with shorter carbon chains, such as methanol and ethanol, are more effective at increasing the ionic conductivity than longer-chain alcohols, such as 1-propanol and 1-butanol. This can be explained by the fact that shorter-chain alcohols are more polar and have smaller molecular sizes, allowing them to more readily integrate into the DES structure and interfere with the hydrogen bonding network. Their smaller size also means that they can better interact with and solvate the ions in the DES, further enhancing the ionic conductivity (Kumar et al., 2022). In contrast, longer-chain alcohols are less polar and larger, which means that they are less effective at disrupting hydrogen bonds and may even contribute to an increase in viscosity, thereby having a less significant effect on conductivity (Azmi et al., 2022; Kumar et al., 2022).

Effect of the addition of alcohol to DESs on electrochemical stability

Fig. 4 shows the current response of a DES (deep eutectic solvent) and DES mixtures with 5% methanol, ethanol, and 1-propanol as a function of applied potential. CV analysis revealed that adding short-chain alcohols (methanol, ethanol, and 1-propanol) to the DES did not significantly impact its oxidative stability, as indicated by the consistent onset of oxidation at approximately 1 V across all the samples. This stability suggests that these alcohols do not introduce new electrochemical activity within the DES operational window, which aligns with findings that show similar stability in DESs with inert additives (Bučko et al., 2018).

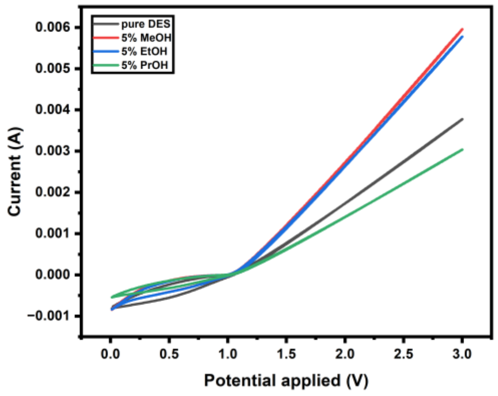

Figure 4. CV of DESs and DESs with 5% alcohol addition

Moreover, compared with the pure DES and DES with 1-propanol mixtures, the methanol and ethanol mixtures resulted in a steeper current increase, indicating improved ionic conductivity. This enhancement is likely due to the polar nature and smaller molecular size of methanol and ethanol, which disrupt the hydrogen bond network, reduce viscosity and enable greater ion mobility, as supported by a previous study (Monteiro et al., 2022). In contrast, the larger molecular size and lower polarity of 1-propanol reduce its effectiveness in disrupting hydrogen bonds, resulting in a lower current response and thus less impact on ionic conductivity.

CONCLUSION

This study investigated the synthesis and optimization of a deep eutectic solvent (DES) composed of choline chloride and urea, focusing on molar ratios, viscosity, ionic conductivity, and electrochemical stability upon alcohol addition. The 1:2 molar ratio of choline chloride to urea emerged as the optimal composition, achieving complete dissolution and forming a stable, transparent solution that maximized hydrogen bonding within the DES structure. Short-chain alcohols, particularly methanol and ethanol, significantly reduce DES viscosity and enhance ionic conductivity by disrupting the hydrogen bond network, facilitating ion mobility. The small molecular size and high polarity of these alcohols allow them to integrate effectively into DESs, lowering their viscosity and improving their conductivity. In contrast, larger alcohols, such as 1-propanol and 1-butanol, were less effective at altering these properties and, in some cases, increased viscosity because of their weaker interactions with the DES matrix. Electrochemical analysis demonstrated that the addition of 5% short-chain alcohols did not alter the oxidative stability of the DES, with the oxidation potential remaining consistent at approximately 1 V. This finding indicates that these alcohols do not introduce additional redox activity, preserving the electrochemical stability window of the DES.

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