**A Novel Potassium Chloride Based Natural Deep Eutectic Solvent: In-House Synthesis and Characterization**

**Muhammad Hammad Rasool**1*, Maqsood Ahmad2**, Syed Abdul Moiz Hashmi3

1*,2** Petroleum Geosciences Department, Universiti Teknologi Petronas, Bandar Seri Iskandar, Malaysia  
3 Chemical Engineering Department, Universiti Teknologi Petronas, Bandar Seri Iskandar, Malaysia

*Corresponding author, Email address: muhammad_19000949@utp.edu.my  
**Corresponding author, Email address: maqsood.ahmad@utp.edu.my

**Received** 16 May 2023,  
**Revised** 08 July 2023,  
**Accepted** 10 July 2023


**Abstract:** The increasing use of Ionic Liquids (ILs) and Deep Eutectic Solvents (DES) for their eco-friendly properties and versatile applications has been tempered by recent findings exposing their sustainability limitations. As a response, a new type of DES called Natural Deep Eutectic Solvents (NADES) has emerged, offering similar efficiency to ILs and DES but with improved environmental credentials. This study presents the synthesis and characterization of a novel Natural Deep Eutectic Solvent (NADES) based on Potassium Chloride (KCl) and glycerine. A eutectic mixture is achieved with a 1:8 molar ratio of KCl to glycerine at 70°C and 100 rpm. Thermophysical properties, including density, surface tension, viscosity, refractive index, and pH, are measured over a temperature range of 289.15 K to 333.15 K. Fourier Transform Infrared (FTIR) analysis confirmed the bonding between the Cl- from KCl and -OH group from glycerine. Thermogravimetric analysis revealed thermal stability of up to 200°C for the NADES. The results demonstrated the potential of this newly developed KCl-based NADES as a sustainable alternative to Ionic Liquids (ILs), Deep Eutectic Solvents (DES), and KCl salt in various applications. Further research is recommended to explore its efficacy in different fields.

**Keywords:** NADES; DES; Ionic Liquids; Potassium Chloride; Natural Materials

1. **Introduction**

Ionic liquids have gained popularity as solvents in various fields such as electrodeposition, electropolishing, and biotransformations due to their versatile applications (Kaur, Kumar et al. 2022; Pei, Zhang et al. 2022). However, recent research has revealed that ionic liquids containing Imidazolium-based cations are often toxic, and they are generally considered expensive, non-biodegradable, and difficult to prepare (Leitch, Abdelghany et al. 2020; Messali et al. 2014). As a result, the search for a cheaper, non-toxic, and equally effective alternative to ionic liquids has intensified (Perna, Vitale et al. 2020, El Achkar, Greige-Gerges et al. 2021, Rasool, Zamir et al. 2021). This quest has led researchers to explore Deep Eutectic Solvents (DES) as a viable option in many applied fields (Rasool, Ahmad et al. 2022). DES are essentially a combination of Hydrogen Bond Donor (HBD) and Hydrogen Bond Acceptor (HBA) that are mixed at specific compositions and temperatures to form a eutectic mixture, as depicted in Figure 1. The depression in melting point of a eutectic mixture compared to that of the pure materials is believed to be due to the charge delocalization.
from HBA to HBD facilitated by hydrogen bond formation (Rasool, Zamir et al. 2021, Rasool, Ahmad et al. 2022). Additionally, the strength of hydrogen bonds at the eutectic point must be balanced by a reduction in cohesive interactions. Factors such as the lattice energies of HBA and HBD, entropy changes upon DES formation, and the interaction between the anion and HBD also play crucial roles in the melting point depression of DES (Rahman, Roy et al. 2021, Rasool and Ahmad 2023).

![Eutectic composition and temperature graph](Rasool and Ahmad 2023)

Although Deep Eutectic Solvents (DES) are often considered a greener alternative to Ionic Liquids, it is worth noting that DES can still contain toxic components, such as ammonium-based salts used as hydrogen bond acceptors. This raises questions about the true environmental friendliness of DES. In response to this concern, Natural Deep Eutectic Solvents (NADES), which are derivatives of DES, have emerged as a potential solution (Rasool, Ahmad et al. 2023). NADES are still considered DES, but their components are naturally occurring substances, such as potassium chloride, calcium chloride, and Potassium chloride salt (Russo, Tiecco et al. 2022). With millions of possible combinations of DES and NADES available, there is a need for further research to explore their efficacy and potential applications in various fields (Arkawazi, Barzinjy et al. 2021). In this study, Potassium chloride salt, will be used as a hydrogen bond acceptor, and glycerine will be used as a hydrogen bond donor due to its high total hydrogen bond count and polarity of functional group.

Potassium chloride (KCl) is a naturally occurring compound that is widely used in various applications. It is a white crystalline powder or colorless crystal with a salty taste, and it is soluble in water (Abiandu and Ita 2019). Potassium chloride is commonly used as a salt substitute in food and beverages for individuals who need to reduce their sodium intake. It is also used as a fertilizer in agriculture due to its high potassium content, which is an essential nutrient for plant growth. In addition, potassium chloride is used in medical settings as a source of potassium for intravenous infusions to treat potassium deficiencies in patients. It is also used in pharmaceuticals, scientific research, and other industrial processes. Potassium chloride is an important compound with diverse applications in various fields. In short, it has tremendous applications where it is required in large concentration, however, in this study, a potassium chloride and glycerine based NADES has been prepared which is recommended to be used as a more viable alternative of potassium chloride salt in smaller concentration.
2. Materials and Methods

2.1. Materials
Anhydrous Potassium chloride Salt 99%> and Glycerine (99USP) have been acquired from Sigma Aldrich, Malaysia.

2.2. Methods

2.2.1. In-house Preparation
Potassium chloride salt and glycerine were mixed at varying molar ratios, as depicted in Table 1, to obtain a eutectic mixture. The formation of a eutectic mixture was confirmed visually by observing a homogeneous and transparent liquid with no turbidity, indicating that the hydrogen bond donor (HBD) and hydrogen bond acceptor (HBA) were mixed at the eutectic composition (Mudzakir, Jafarian et al. 2022). Preliminary experiments were conducted to investigate the temperature dependence of the mixing pattern of HBD and HBA. Eutectic mixture ratios were tested at two different temperatures:, 70°C, and above 80°C, as per literature indicating that the eutectic temperature for most deep eutectic solvents (DES) falls between 50°C and 80°C (El Achkar, Greige-Gerges et al. 2021). It was observed that at 70°C, precipitation and turbidity occurred at all molar ratios, and 80°C, the mixture became somehow thick and burnt. Therefore, in this paper, only the properties of natural deep eutectic solvents (NADES) formulated at the eutectic temperature (70 °C), as shown in Table 1, are discussed in Section 3. The METTLER Digital Balance was used for weighing HBD and HBA, while the Thermo Fisher Hot plate was utilized for controlled heating and stirring of HBD and HBA at 100 rpm.

2.2.2. Thermo-physical and chemical characterization
The thermophysical properties, including density, surface tension, refractive index, pH and viscosity, of the NADES prepared in-house were measured within the temperature range of 289.15 K to 333.15 K, primarily due to equipment limitations. To assess the thermal stability of the newly prepared NADES, thermogravimetric analysis (TGA) was conducted. Additionally, FTIR and pH measurements will be employed for chemical characterization of the NADES.

2.2.2.1. Density
The density of the newly prepared NADES was determined using a DMA 35 Basic handheld density meter within the temperature range of 289.15 K to 333.15 K. Due to the absence of an in-built heating mechanism in the density meter, the NADES was heated separately to the desired temperature (± 2 OC), and then a 2 ml sample was drawn through the pipette and the density was directly displayed on the screen. It should be noted that a margin of error of ± 2 °C is expected due to the absence of an in-built heating mechanism.

2.2.2.2. pH
The pH of the newly prepared NADES was measured using a Kenis desktop pH meter within the temperature range of 289.15 K to 333.15 K. Since the pH meter does not have an in-built heating mechanism, the NADES was heated separately using a hot plate to the desired temperature (± 2 °C). The pH meter probe was then immersed directly into the NADES, and the pH value was noted when the reading stabilized.

2.2.2.3. Surface Tension
The surface tension of the newly prepared NADES was measured using an Interfacial Tension Meter (IFT700) within the temperature range of 289.15 K to 333.15 K. A droplet of NADES was formed in a chamber containing the bulk fluid using a capillary needle, at the desired temperature and pressure.
conditions. The latest image capturing and processing system were used to input the relevant geometric parameters, which were then used to calculate the interfacial tension using the Laplace equation.

2.2.2.4. Refractive Index
The refractive index of the newly prepared NADES was determined using an ATAGO refractometer within the temperature range of 289.15 K to 333.15 K. Refractometers measure the angle of refraction, which indicates the extent to which light changes direction. The ATAGO refractometer is equipped with a thermo-module that regulates temperature, eliminating the need for a separate water bath to maintain a constant temperature. To measure the refractive index, the prism surface of the refractometer is cleaned with a clean cloth or lens paper to remove any residue or dirt. Then, a few drops of the sample solution are placed on the prism surface and spread evenly. The refractometer is calibrated using a known reference solution, such as distilled water or a standard sugar solution, and the refractive index is read from the screen.

2.2.2.5. Viscosity
The viscosity of the newly prepared NADES was measured using a Brookfield Rotational Viscometer (Low Temperature model) with a shear rate of 30 rpm and a spindle size of 6, within the temperature range of 289.15 K to 333.15 K. The Brookfield viscometer measures viscosity by detecting the torque required to rotate a spindle at a constant speed while it is submerged in the sample fluid. The sample is placed on the screen just below the spindle, and the spindle is tightened to cover the entire surface of the sample. The viscometer measures the torque needed to maintain the spindle at a constant speed, which is directly proportional to the viscosity of the sample. The Brookfield Viscometer displays the viscosity of the sample in centipoise (cP).

2.2.2.6. Thermogravimetric Analysis (TGA)
The thermal stability of the NADES was determined using a Thermogravimetric Analyzer (TGA). The TGA measures the change in mass of a sample as it is heated. The heating process is precisely controlled, and the mass loss or gain of the sample is plotted as a function of temperature. The NADES sample is first prepared by thorough mixing and homogenization, and any surface moisture is removed. The sample is then placed in a TGA pan, typically made of an inert material like aluminum. The TGA instrument is calibrated with a reference material, such as a weighed standard, to ensure accurate results. The TGA experiment involves heating the sample in a controlled manner, usually at a constant heating rate, typically 0.1 °C/min, over a temperature range of 0-500 °C. The weight of the sample is continuously monitored as a function of temperature, and the TGA instrument collects data on temperature, weight, and other parameters such as gas flow or sample temperature. Once the TGA experiment is completed, the data can be analyzed to determine the weight loss or gain of the sample as a function of temperature. This information can be used to identify the temperature range at which the sample undergoes physical and chemical transformations, such as melting, evaporation, oxidation, or decomposition.

2.2.2.7. Fourier Transform Infrared spectroscopy (FTIR)
Fourier Transform Infrared (FTIR) spectroscopy is a technique that uses the infrared section of the electromagnetic spectrum to characterize materials based on the absorption of infrared frequencies by the vibrational frequencies of chemical bonds in their molecular structures. Raw data obtained from FTIR spectroscopy is processed using a technique called Fourier Transform to generate an FTIR spectrum.
In the case of NADES, the FTIR analysis is conducted using the KBr pellet method. To set up the equipment, the optics are aligned, the software is configured, and a KBr pellet press is installed. The FTIR instrument is calibrated using a reference material, such as a calibration gas or a reference spectrum, to ensure accurate results. The FTIR instrument then collects data on the infrared absorption or emission spectrum of the NADES sample as a function of wavelength. This data can provide valuable information about the molecular composition and chemical bonds present in the NADES sample.

3. Results and Discussion

3.1. Synthesis of Potassium chloride Salt:Glycerine - NADES

The HBA (Potassium chloride salt) and HBD (Glycerine) have been mixed at various molar ratios at different temperature by mixing at 100 rpm as shown in Figure 2 and Table 1. The experimentation shows that the eutectic mixture has been obtained at 70 °C when HBA and HBD are mixed with molar ratios of 1:2 as shown by Figure 2. At higher temperatures above 80 °C, it was observed that the mixture started burning into dark brownish tar like slurry with bubbles. By Figure 2, the eutectic mixture will only be obtained at eutectic temperature and eutectic mole ratio. If the mixing is taking place at hypoeutectic and hypereutectic conditions, either the mixture will turn out cloudy or there will be precipitate formed as shown in Figure 2 for non-eutectic molar ratios i.e. 1:1, 1:2, 1:3, 1:4, 1:5, 1:6, 1:7, 2:2 where mixture either turned out to be light cloudy, intense cloudy or showed intense precipitation. The eutectic mixture is obtained at 1:8 molar ratio.

Figure 2: Mixing of KCl:Glycerine at various molar ratios

Table 1: Eutectic and Non-Eutectic compositions of KCl based NADES

<table>
<thead>
<tr>
<th>KCl : Gly molar ratio</th>
<th>Observation</th>
<th>Confirmation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>Turbid, white, precipitate</td>
<td>Non- Eutectic mixture</td>
</tr>
<tr>
<td>1:2</td>
<td>Turbid, white, precipitate</td>
<td>Non- Eutectic mixture</td>
</tr>
<tr>
<td>1:3</td>
<td>Turbid, white, precipitate</td>
<td>Non- Eutectic mixture</td>
</tr>
<tr>
<td>1:4</td>
<td>Turbid, precipitate</td>
<td>Non- Eutectic mixture</td>
</tr>
<tr>
<td>1:5</td>
<td>Turbid, precipitate</td>
<td>Non- Eutectic mixture</td>
</tr>
<tr>
<td>1:6</td>
<td>Transparent with precipitate</td>
<td>Non- Eutectic mixture</td>
</tr>
<tr>
<td>1:7</td>
<td>Transparent with precipitate</td>
<td>Non- Eutectic mixture</td>
</tr>
<tr>
<td>1:8</td>
<td>Transparent, no precipitate</td>
<td>Eutectic mixture</td>
</tr>
<tr>
<td>2:2</td>
<td>Intense cloudy</td>
<td>Non- Eutectic mixture</td>
</tr>
<tr>
<td>2:3</td>
<td>Intense cloudy</td>
<td>Non- Eutectic mixture</td>
</tr>
</tbody>
</table>

3.2. Effect of temperature on density
It is very significant to know the density behavior of NADES before its utilization in different studies. The density of KCl-NADES was determined to be 1.282 g/cc (Figure 3). This information provides insights into the compactness and mass per unit volume of the NADES, which can have implications on their behavior in different applications. For example, higher density NADES may have different buoyancy characteristics or settling rates compared to lower density NADES, which can impact their performance in specific applications.

The observed density of the potassium chloride salt-based NADES is higher than that of raw glycerin, which can be attributed to the addition of the hydrogen bond acceptor, potassium chloride salt, in glycerin. The density of KCl-NADES decreases to 1.2 g/cc at 60°C, as the temperature increases (Figure 3). This decrease in density is attributed to the spreading out of NADES molecules due to the increase in kinetic energy of the system upon heating, resulting in a larger volume occupied by the DES molecules and thus a lower density. The relationship between density and temperature in NADES is found to be rather linear and can be mathematically represented by equation (1). The density of NADES is shown in Figure 3, with an Absolute Mean Percentage Error (AMPE) of 1.1% and error bars drawn with a 5% error margin, indicating the precision of the measurements:

\[ \rho = -0.0024T + 1.3448 \]  \hspace{1cm} (1)

3.3. Effect of Temperature on pH
The negative log of hydrogen ion concentration in any solution is attributed by its pH values. It is very important to know the pH of NADES before its implication in pH sensitive applications such as DNA synthesis etc. The pH of KCl-NADES was measured to be 5.69 (Figure 4), indicating that it is slightly acidic. This information is important as it can affect the chemical reactivity and stability of NADES, as well as their compatibility with other materials or processes. For instance, in applications where a certain pH range is desired, such as in pharmaceuticals or food processing, the pH of NADES can be a critical parameter to consider. The pH of NADES and its temperature dependency is shown in Figure 4 and eq (2), with an Absolute Mean Percentage Error (AMPE) of 0.5% and error bars drawn with a 5% error margin, indicating the precision of the measurements:

\[ pH = -0.0018T + 5.7325 \]  \hspace{1cm} (2)
3.4. Effect of Temperature on surface tension

Surface tension is the ability of liquid surfaces to occupy as minimum surface area as possible. It is very significant to evaluate the surface tension of NADES before utilizing them in applications which depend upon capillary pressure. Surface tension of NADES has been found between 25 °C and 60 °C. At 25 °C, the surface tension of KCl-NADES was found to be 59.4 mN/m (Figure 5). Surface tension is a measure of the cohesive forces within a liquid and can impact its behavior in terms of wetting, spreading, and capillary action. The surface tension of NADES can have implications in various applications, such as in coatings, emulsions, or foams. Understanding the surface tension of NADES can provide insights into their interfacial properties and potential performance in specific applications (Chen, Chen et al. 2019). The surface tension of studied NADES non-linearly decreases which can be mathematically shown by eq (3). The surface tension of the studied NADES has been reported in Figure 4 with AMPE of 1.2%.

\[
\sigma = -0.0031T^2 + 0.0689T + 59.378 \\
(3)
\]

3.5. Effect of temperature on refractive index

The refractive index of KCl-NADES was determined to be 1.445 (Figure 6). The refractive index is a measure of how much a substance bends light and can impact the optical properties of NADES, such as their transparency, light scattering, or refractive behavior. Knowledge of the refractive index of
NADES is important in applications such as optics, sensors, or imaging where their optical properties play a crucial role (Chen, Zhao et al. 2022). The refractive index of the NADES decreases non-linearly with temperature as shown in eq(4) and Figure 6 with 0% AMPE. At elevated temperature, the liquid becomes less viscous and dense, which causes the light to travel faster in the medium, resulting into small values of ‘n’.

\[ n = 0.00005T^2 - 0.0016T + 1.4776 \]  

\[ \mu = -0.0295 T^2 - 4.3317T + 1035.7 \]  

3.6. Viscosity
The viscosity of KCl-NADES was measured to be 994 cp at 25°C (Figure 7), which is slightly higher than that of glycerine. Viscosity is a measure of a liquid's resistance to flow and can impact its handling, processing, and flow behavior in various applications. Understanding the viscosity of NADES is important for predicting their flow characteristics, stability, and performance in processes such as mixing, pumping, or coating. The decrease in viscosity with the increase in temperature is mainly due to decline in intermolecular attraction which renders the liquid less viscous as shown in Figure 7 and eq (5) where the viscosity declines to 898 cp at 60 °C with overall AMPE of 1.8%.

\[ y = -0.0031x^2 + 0.0689x + 59.378 \]  

\[ y = 1E-05x^2 - 0.0016x + 1.4776 \]
Overall, the determination of thermophysical properties such as density, pH, surface tension, refractive index, and viscosity of KCl-NADES provides valuable information for understanding their behavior and potential applications in different industries. The results obtained from these measurements can be used to optimize their performance, tailor their properties to specific applications, and guide further research and development in the field of NADES.

3.7. TGA

Thermogravimetric analysis (TGA) has been performed on NADES, as depicted in Figure 8. The TGA curve in Figure 8 indicates that the main weight loss of NADES occurs after 200°C. Since the melting point of KCl is 770°C (Kaniewski, Hoffmann et al. 2019), the weight loss is primarily attributed to the degradation of glycerin at higher temperatures, specifically between 200°C to 350°C, where glycerin is converted into formaldehyde.

Figure 7: Viscosity of Potassium chloride salt based NADES

![Viscosity of Potassium chloride salt based NADES](image)

\[ y = 0.0295x^2 - 4.3317x + 1035.7 \]

Figure 8: TGA of Potassium chloride salt based NADES

![TGA of Potassium chloride salt based NADES](image)
3.8. FTIR
Fourier Transform Infrared (FTIR) spectroscopy was conducted to investigate the formation of bonds between KCl and glycerin in NADES. The FTIR spectra showed characteristic peaks of KCl at 1394 cm^-1, while the peak at 3317 cm^-1 was attributed to adsorbed moisture as OH stretching (Wang, Lee et al. 2020, Maquirriain, Neyertz et al. 2022). Glycerin exhibited a peak related to -OH bending at 1414 cm^-1. In NADES, a corresponding peak shift was observed at 1410 cm^-1, indicating a change in wavenumber due to differences in electronegativity, which suggests the formation of a new bond. The shift from 1414 cm^-1 to 1410 cm^-1 indicates that glycerin has reacted with KCl, and the -OH group, which acts as a hydrogen bond donor, has formed a bond with chloride in KCl, as illustrated in Figure 9.

![FTIR spectra](image)

Figure 9: FTIR of Potassium chloride salt based NADES

4. Way Forward
The newly prepared natural deep eutectic solvent (NADES) with potassium chloride (KCl) can have several potential uses in various fields due to its specific properties. Here is a way-forward featuring utilization of this newly prepared NADES in various applied fields:

**Electrochemistry**: The NADES can be used as an electrolyte in electrochemical applications, such as batteries, capacitors, and electroplating, due to its ionic nature and good thermal stability (Abbott 2022).

**Chemical synthesis**: The NADES can be used as a reaction medium or solvent in chemical synthesis processes, especially for reactions that require mild conditions or are sensitive to water or organic solvents. The NADES can provide a suitable environment for specific reactions, such as enzyme-catalyzed reactions, due to its unique physicochemical properties (Yu, Xue et al. 2022).

**Pharmaceutical industry**: The NADES can be used as a solvent or carrier for drug delivery systems, due to its biocompatibility and ability to solubilize a wide range of polar and non-polar drugs. It can also be used in formulation of pharmaceuticals, cosmetics, and personal care products (Pedro, Freire et al. 2021).

**Agriculture**: The NADES can be used as a foliar spray or soil conditioner in agriculture to enhance nutrient uptake, improve plant growth, and increase crop yield. Its low toxicity and environmentally friendly properties make it a potential alternative to conventional chemical fertilizers (Socas-Rodríguez, Torres-Cornejo et al. 2021).
Food industry: The NADES can be used as a solvent or additive in food processing for extraction, preservation, and flavor enhancement purposes. It can also be used as a natural food preservative due to its antimicrobial properties and low toxicity (Mišan, Nadpal et al. 2020).

Green chemistry: The NADES can be used as a sustainable and environmentally friendly alternative to conventional organic solvents in various green chemistry processes, such as extraction, catalysis, and separation. Its low toxicity, biodegradability, and renewable nature make it a promising candidate for green chemistry applications (Santos, Assis et al. 2022).

Optical industry: The NADES can be used as a refractive index matching medium or optical adhesive in optical devices, such as lenses, optical coatings, and sensors, due to its refractive index close to that of glass (1.445) (Pidenko, Vakh et al. 2021).

Energy storage: The NADES can be used as a medium for thermal energy storage or heat transfer fluid in solar thermal systems or other thermal energy storage technologies, due to its high thermal stability and density (Azmi, Koudahi et al. 2022).

CO₂ storage and capture: NADES can capture CO₂ through a process called chemical absorption. NADES based KCl can act as a solvent to selectively absorb CO₂ from flue gases or other emission sources due to their high polarity and ionic nature. The CO₂ molecules dissolve in the NADES, forming a stable compound, which can be separated and stored for further utilization or sequestration. Moreover, NADES can potentially be used as a medium for CO₂ storage due to their ability to dissolve and stabilize CO₂. Once CO₂ is captured and absorbed in NADES, it can be stored in suitable reservoirs, such as underground geological formations or other storage sites, as a means of long-term carbon sequestration (Rasool, Ahmad et al. 2023).

These are just a few potential applications of the newly prepared NADES with potassium chloride. Further research and development can explore more possibilities and optimize the utilization of this unique solvent in various fields.

4. Conclusion
   1. Potassium chloride salt and Glycerine have been selected based upon total hydrogen bond count and is concluded to be utilized as a potential alternative of potassium chloride salt.
   2. Eutectic mixture is achieved at 70 °C, when mixed with molar ratios of 1:8.
   3. Thermophysical properties of KCl based NADES decline with increase in temperature. It is observed that Potassium chloride salt based NADES is denser and more viscous than glycerine, is slightly acid and possess high refractive index as compared to glycerine.
   4. Potassium chloride salt based NADES is stable up to 200 °C which makes it suitable for high temperature applications.
   5. A way forward has been suggested which recommends Potassium chloride salt based NADES to be utilized in various applications.

Acknowledgement: The authors would like to thank YUTP grant 015LC0-326 for the financial support for this research work.

Disclosure statement: Conflict of Interest: The authors declare that there are no conflicts of interest.

Compliance with Ethical Standards: This article does not contain any studies involving human or animal subjects.

References


(2023) ; https://revues.imist.ma/index.php/morjchem/index