A Novel Ascorbic Acid Based Natural Deep Eutectic Solvent as a Drilling Mud Additive for Shale Stabilization

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Abstract: During drilling, almost 70% of wellbore instability issues result from the encountering of shale formations. Various additives such as salts, silicates, and polymers are used in water-based mud to enhance its shale-inhibition capability; however, such additives have certain limitations. Lately, ionic liquids and deep eutectic solvents (DES) have been used by various research groups as shale inhibitors in drilling fluid due to their biodegradability and efficacy. However, their popularity faded when a natural derivative of DES, i.e., Natural Deep Eutectic solvent (NADES), came into the picture. This research utilizes the in-house-prepared Ascorbic acid and Glycerine (AA:Gly)-based NADES as a drilling fluid additive for shale inhibition and compares its efficacy with counterpart inhibitors such as KCl, imidazolium-based ionic liquid, and Choline Chloride-based DES. The results show that 3% NADES improved the overall Yield point to Plastic viscosity ratio, with a 39.69% decline in mud cake thickness and a 28% decline in the filtrate volume of drilling mud. Along with improved drilling fluid properties, 3% NADES resulted in 77.77% shale inhibition and 87% shale recovery. Surface tension, d-spacing, zeta potential, and FESEM have been conducted to justify and elucidate the inherent mechanism behind the working of NADES as a drilling fluid additive and clay stabilizer. Thus, Ascorbic acid-based NADES is recommended as a potential non-toxic and cheap drilling fluid additive to improve drilling fluid properties and clay stability.

Keywords: shale swelling; drilling fluid; clay mineralogy; NADES; ionic liquids

1. Introduction

Shale is a sedimentary rock that is composed of clay, silt and other fine-grained minerals [1]. It is formed by the compression and solidification of sediment, such as clay and silt, over time [2,3]. Shale is an important rock for the oil and gas industry because it often contains hydrocarbons such as natural gas and oil. Shale rock formations are the main target for hydraulic fracturing (fracking) to extract the natural gas and oil that is trapped in the rock [4]. Shale rock is also known to be prone to swelling and breaking when exposed to drilling fluids and changes in pressure, which can cause significant problems during drilling operations, such as stuck pipes, lost circulation and reduced penetration rates [5].

Shale swelling refers to the expansion of shale rock caused by an increase in fluid pressure, fluid content, or changes in temperature. Swelling of shale can cause significant problems during drilling operations, such as stuck pipes, lost circulation, and reduced penetration rates [6]. Shale swelling is caused by the absorption of fluids, such as water, into the rock [7]. This can lead to an increase in the rock’s volume, which can cause the rock to crack, break, or deform. Swelling can also occur due to changes in temperature. When there is an increase in temperature, the rock tends to expand, and when the temperature decreases, contraction occurs [8]. This thermal expansion and contraction can cause the rock
to crack and break, which can cause problems during drilling [9]. There are several methods used to inhibit shale swelling during drilling, including using high-density drilling fluids, adding clay inhibitors, using polymer-based muds, using chelating agents, and using low-permeability muds [10].

Shale swelling inhibitors are chemicals that are added to drilling fluids to prevent the swelling and expansion of shale formations when drilling for oil and gas [11]. This can help to maintain the stability of the wellbore and prevent damage to the surrounding rock. Some common types of shale inhibitors include organophosphates, polysaccharides, and clay stabilizers. These chemicals are typically added in small amounts to the drilling fluid, and their effectiveness can vary depending on the specific type and composition of the shale being drilled [12]. In recent years, Ionic liquids (ILs) have also been studied as potential shale inhibitors by the oil and gas industry [13]. Ionic liquids (ILs) are a class of compounds that consist of organic cations and inorganic or organic anions [14]. They are characterized by their low vapor pressure and high thermal stability, which make them suitable for use as solvents and catalysts in various industrial processes [15]. The unique properties of ILs, such as their tunable viscosity, low toxicity, and biodegradability, make them a promising alternative to traditional shale inhibitors. ILs can effectively reduce the swelling and expansion of shale formations, which can help to improve the stability of the wellbore and prevent damage to the surrounding rock [16,17].

In a study by Rahman et al. (2022), the researchers utilized tetramethylammonium chloride (TMACl) and 1-ethyl-3-methylimidazolium chloride (EMIMCl) in drilling mud and found that they led to 23.40% and 15.66% reductions in linear swelling, respectively [18]. Rizwan et al. (2021) found that using Trihexyltetradecyl phosphonium bis(2,4,4-trimethyl pentyl) phosphonate-based ionic liquid resulted in 12.3% shale inhibition compared to water. Huang et al. (2020) found that using ionic liquids such as 1-hexyl-3-methylimidazolium bromide and 1,2-bis(3-hexylimidazolium1-yl) ethane bromide with Na-Bt pellets led to 86.43% and 94.17% reductions in shale swelling, respectively [19]. Yang et al. (2019) used 1-Vinyl-3-dodecylimidazolium bromide and 1-Vinyl-3-tetradecylimidazolium bromide and found that they led to 16.91% and 5.81% reductions in shale swelling, respectively [20].

In another study by Ofei et al. (2017), the researchers used 1-butyl-3-methylimidazolium chloride (BMIM-Cl) in water-based mud, which resulted in a reduction in mudcake thickness of up to 50% and decreased YP/PV at all considered temperatures, improving the overall efficiency of the drilling fluid [21]. Yang et al. (2017) found that using 1-Vinyl-3-ethylimidazolium bromide led to a 31.62% reduction in shale swelling with a 40.60% shale recovery rate [22]. Lastly, Luo et al. (2017) found that using 1-octyl-3-methylimidazolium tetrafluoroborate resulted in an 80% reduction in shale swelling [22].

Ionic liquids (ILs) have several potential disadvantages as shale inhibitors for the oil and gas industry [23–26]. High cost: ILs are relatively expensive compared to traditional shale inhibitors, which can make them less cost-effective for large-scale drilling operations. Handling and storage: ILs are liquid at room temperature, which can make them difficult to handle and store. They are also hygroscopic, meaning they absorb moisture from the air, which can affect their performance. Environmental impact: ILs are considered to be less toxic and more biodegradable than traditional shale inhibitors, but their environmental impact is not well understood. Compatibility: ILs may not be compatible with other chemicals used in drilling fluids, which can limit their effectiveness or cause unexpected reactions. Toxicity: Some Ionic liquids are toxic and can be dangerous if not handled correctly. This motivated various researchers to exploit the applications of Deep Eutectic Solvent (a non-toxic alternative of ionic liquids) in drilling fluids.

Deep Eutectic Solvent (DES) is typically formulated by mixing a low-melting-point, hydrogen-bond-donating compound (called the hydrogen bond acceptor or HBA) with a high-melting-point, hydrogen-bond-accepting compound (called the hydrogen bond donor or HBD) [27,28]. The mixture of these two compounds forms a new solvent with properties that are different from the individual components. The process of formulating a DES is relatively simple and can be done by mixing the HBA and HBD compounds in a desired
molar ratio, and then heating the mixture until it becomes a homogeneous liquid [29]. The heating process helps to break any existing hydrogen bonds between the HBA and HBD molecules, allowing them to form new, stronger hydrogen bonds with each other.

DESs are generally cheaper and easier to prepare than ionic liquids, as they can be made by mixing simple and readily available compounds, while ionic liquids often require more complex and costly precursors. DESs are often more environmentally friendly than ionic liquids, as they are typically made from biodegradable or non-toxic ingredients. DESs have a lower toxicity than ionic liquids, making them safer to handle and dispose of. DESs have a more favorable toxicity profile compared to ionic liquids, which can be toxic or corrosive in some cases. It is worth noting that both ionic liquids and DESs have their own unique properties, and the choice of which one to use will depend on the specific application and the requirements of the research.

Han Jia et al. (2019) were among the first to use DES as shale inhibitors. They used Propanoic acid ChCl (1:1), 3-phenyl propanoic acid ChCl (1:2), and 3-mercapto propanoic acid + Itaconic acid + ChCl (1:1:2)-based DES and found that they provided 68%, 58%, and 58% bentonite swelling inhibition, respectively [30]. M.H. Rasool et al. (2021) used a Glycerine:Potassium Carbonate DES (2:1) for a free-style experiment using swelling shale samples and obtained 87% swelling inhibition [31,32]. Jingua Ma (2020) used a Urea:ChCl-based DES and achieved 67% shale swelling inhibition [33]. M.H. Rasool et al. (2022) used a double action P-D inhibitor combination of Potassium carbonate-based DES and Poly (2-ethyl-2-Oxazoline) hydroxyl-terminated polymer in drilling mud, resulting in 76% swelling inhibition [34].

Natural Deep Eutectic Solvents (NADESs) are a subcategory of DESs that are formulated from natural and biodegradable compounds [35]. A NADES is a type of eutectic mixture made from natural, renewable resources such as sugars, amino acids, and organic acids. These mixtures can have similar properties to traditional eutectic solvents, which are typically made from synthetic chemicals, but are more environmentally friendly. NADESs have been studied for a variety of applications, including as solvents for organic synthesis, as electrolytes for energy storage devices, and as lubricants [36]. NADESs have become increasingly popular in recent years because they offer several advantages over traditional DESs that are formulated from synthetic compounds [37]. NADESs are considered more environmentally friendly, as they are typically made from biodegradable or non-toxic ingredients, which reduces the environmental impact of their production and disposal. NADESs are often cheaper and easier to obtain than traditional DESs, as they can be made from readily available natural compounds, such as sugars, amino acids, and essential oils. NADESs can be used to improve the solubility of natural compounds and can be used in the extraction and isolation of natural products with high efficiency. NADESs can have wider potential for application than traditional DESs, as they have a lower toxicity and are biocompatible.

This research utilizes an Ascorbic acid:Glycerine (AA:Gly)-based Natural Deep Eutectic solvent as a drilling fluid additive to check its candidacy as a clay stabilizer and shale inhibitor followed by detailed characterizations to understand the underlying mechanism. Moreover, the performance of our novel NADES as a drilling fluid additive will be compared with conventional shale inhibitor KCl and the most utilized ionic liquid (EMIM-Cl) and DES (Choline Chloride:Urea) in drilling fluids. The Ascorbic acid-based NADES was prepared in-house and its basic synthesis is included as a part of this article. However, detailed synthesis and characterization will be published in a subsequent article.

2. Materials and Methods
2.1. In-House Preparation of Ascorbic Acid:Glycerine (AA:Gly) NADES

Different molar ratios of Ascorbic Acid (Vitamin C) and Glycerine were mixed to create a eutectic mixture. This mixture can be identified by its homogenous, transparent appearance and lack of turbidity, indicating that the mixture has reached its eutectic composition. Experiments were conducted to examine the temperature dependence of the
mixing pattern. The eutectic mixture ratios were determined at three temperatures: 50 °C and 80 °C, as the literature suggests that the eutectic temperature typically falls between 50 °C and 80 °C. A METTLER Digital Balance was used to weigh the ingredients and a Thermo Fisher hot plate was used for controlled heating and stirring at 100 rpm. The detailed FTIR, NMR, and other detailed characterization of the in-house prepared NADES will be added in a subsequent article.

2.2. Screening Criteria to Select HBD and HBA for NADES

M.H. screening criteria for the selection of DES as a shale inhibitor has been used to utilize Ascorbic acid and glycerine as the components for NADES. The criteria address the components having higher hydrogen bond count and containing polar functional groups are prone to give better shale inhibition. More details regarding this criterion can be read in our previous work [39]. Further elaboration on Ascorbic acid and Glycerine are provided in Section 3.1.

2.3. Bentonite Wafer Preparation

Bentonite wafers are used in studies of shale swelling because they contain the clay mineral ‘smectite’, which is responsible for the swelling behavior of shale. Additionally, obtaining ‘true’ shale core samples is difficult, as the coring process makes the shale too unstable, and the resulting samples may contain other minerals such as sandstone and limestone. Furthermore, experiments on shale outcrops cannot be performed, as they typically do not contain the smectite mineral. This research uses 2.54-cm diameter, 11.5-g compressed pellets of Na-bentonite powder, which have been compressed at 1600 psi using a hydraulic press. The thickness of the pellets is measured before introducing them into the Linear Swell Meter (LSM) environment. They are then submerged in drilling mud samples (base sample and samples with inhibitors) and the change in thickness is measured by the LSM every 60 s for 24 h.

Composition of Bentonite

XRD of Sodium bentonite is conducted to discover its composition for confirming the presence of the smectite group in the linear swelling test, as shown in Table 1.

Table 1. Sodium Bentonite composition (XRD).

<table>
<thead>
<tr>
<th>Component</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>29%</td>
</tr>
<tr>
<td>Haematite</td>
<td>4.7%</td>
</tr>
<tr>
<td>Carbonates</td>
<td>9%</td>
</tr>
<tr>
<td>Smectite</td>
<td>47%</td>
</tr>
<tr>
<td>Hatrurite</td>
<td>4%</td>
</tr>
<tr>
<td>Na2O</td>
<td>1.83%</td>
</tr>
<tr>
<td>Iron Silicates</td>
<td>2.17%</td>
</tr>
</tbody>
</table>

2.4. Drilling Fluid Preparation

Water-based drilling fluid was designed using API 13B-1 standards and the composition of the mud is given in Table 2.
Table 2. Drilling mud composition.

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight/conc/vol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium Bentonite</td>
<td>22.5 g</td>
</tr>
<tr>
<td>Soda ash</td>
<td>0.25 g</td>
</tr>
<tr>
<td>Caustic Soda</td>
<td>0.25 g</td>
</tr>
<tr>
<td>Distilled water</td>
<td>350 mL</td>
</tr>
<tr>
<td>NADES (A.A: Gly)</td>
<td>1%, 2%, 3%</td>
</tr>
<tr>
<td>KCl</td>
<td>5%</td>
</tr>
<tr>
<td>1-ethyl-3-methylimidazolium chloride (EMIMCl)</td>
<td>3%</td>
</tr>
<tr>
<td>Choline Chloride:Urea (1:2) DES</td>
<td>3%</td>
</tr>
</tbody>
</table>

2.5. Drilling Fluid Properties

The readings of KCl (5%), EMIMCl (3%), CC:Urea (3%), and NADES-based mud samples at different concentrations (1%, 3%, and 5%) were measured using a FANN Viscometer at 3 rpm, 6 rpm, 300 rpm, and 600 rpm, both before and after aging, at 100 °C and 150 °C. The mud samples were aged by keeping them in a rolling oven at 1000 psia for 24 h. The measurements were used to calculate the Yield Point (YP) and Plastic Viscosity (PV) of the samples using API 13B-1 standards.

2.6. Filtration Properties

HPHT (High Pressure High Temperature) filter press was used to measure the mud cake thickness and filtrate volume of KCl (5%), EMIMCl (3%), CC:Urea (3%), and NADES-based mud samples at different concentrations (1%, 3%, and 5%) at 500 psia, 150 °C for aged and non-aged samples, following API 13B-1 standards.

2.7. Linear Swell Meter

The Grace HPHT (High Pressure High Temperature) Linear Swell Meter (M4600) is a specialized device that measures the change in thickness of a sample, allowing for direct evaluation of shale swelling inhibition properties of water-based drilling fluids. It consists of two parts: a Wafer Compactor and the Linear Swell Meter (Model: M4600). Bentonite wafers were created using the Grace core/wafer compactor and the swelling tests were performed using the Linear Swell Meter (LSM), which provides real-time data on the swelling as conducted, following API 13B-1 standards.

2.8. Shale Recovery Test

A shale outcrop sample was obtained from Niah, District of Miri, Sarawak, Malaysia. The sample was analyzed using X-ray diffraction (XRD) to determine the clay composition and evaluate its suitability for dispersion/shale recovery tests. Table 3 shows the clay mineralogy of the shale samples used in this research. Shale contains high amount of illite and kaolinite, which makes it a dispersive shale that is suitable for shale recovery studies.

Table 3. Clay (Content) mineralogy of shale samples (XRD analysis).

<table>
<thead>
<tr>
<th>Clay Minerals</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Illite</td>
<td>18</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>31</td>
</tr>
<tr>
<td>Chlorite</td>
<td>22</td>
</tr>
<tr>
<td>Vermiculite</td>
<td>10</td>
</tr>
<tr>
<td>Mica</td>
<td>19</td>
</tr>
</tbody>
</table>
2.9. Surface Tension

Surface tension refers to the tension present on the surface of a liquid due to cohesive forces. The capillary action causes water cations to invade the shale’s micropores and is directly proportional to the surface tension. The surface tension of KCl (5%), EMIMCl (3%), CC:Urea (3%), and NADES-based mud samples at different concentrations (1%, 3%, and 5%) was measured using an Interfacial tensiometer (IFT), following ISO 6295.

2.10. XRD

d-spacing is the distance between the alumino-silicate layers in clay and one alumino-silicate layer. X-ray diffraction (XRD) analysis was used to examine the intercalation of inhibitors into the bentonite layers using dry sodium bentonite, base mud, and wet drilling mud samples with incorporated KCl (5%), EMIMCl (3%), CC:Urea (3%), and NADES at different concentrations (1%, 3%, and 5%). A benchtop X-ray diffractometer (D2 phaser) operating at a current of 40 mA and 45 kV with Cu-Kα radiation (λ = 1.54059 Å) was used to obtain XRD peaks for all wet and dry samples. Na-Bt. Bragg’s equation was then applied to calculate the d-spacing as also mentioned in ISO/TS 21236-1.

2.11. FESEM

FESEM (Field Emission Scanning Electron Microscopy) of KCl (5%), EMIMCl (3%), CC:Urea (3%), and NADES-based mud samples at different concentrations (1%, 3%, and 5%) of modified bentonite wafer were used to study the microstructural changes in bentonite clay particles after being treated with various inhibitors. The FESEM images can show the surface morphology of the clay particles, including any changes in shape, size, and surface features. One potential use of FESEM in studying DES-modified bentonite is to investigate how the DES interacts with the clay particles at a microstructural level. For example, FESEM images can show how the DES molecules adsorb onto the clay surfaces, and how this adsorption affects the overall surface chemistry and morphology of the clay particles (ISO 16000-27).

2.12. Zeta Potential

The Malvern Zetasizer was used to measure the zeta potential of KCl (5%), EMIMCl (3%), CC:Urea (3%), and NADES-based mud samples at different concentrations (1%, 3%, and 5%). It is a laser-based system that uses the principle of dynamic light scattering (DLS) to measure the electrophoretic mobility of particles suspended in a liquid. The Zetasizer measures the rate at which the particles move in response to an applied electric field, which is then used to calculate the zeta potential (ISO 13099).

3. Results

3.1. In-House Preparation of NADES

Ascorbic acid and Glycerine were chosen as components for NADES using M.H. screening criteria. Ascorbic acid (Vitamin C) is considered as a hydrogen bond acceptor. It has a total of two potential hydrogen bond acceptor sites, one on the carbonyl oxygen atom, and the other on the hydroxyl (-OH) group [40]. The carbonyl oxygen atom can participate in hydrogen-bonding interactions with other molecules through the partial negative charge on the oxygen atom, while the hydroxyl group can participate in hydrogen bonding through the lone pair of electrons on the oxygen atom.

Glycerol, also known as glycerine, is a trihydroxy alcohol that is a common ingredient in many products, such as food, cosmetic, and pharmaceutical products. It is considered a hydrogen bond donor. It has a total of three potential hydrogen bond donor sites, one on each of the hydroxyl (-OH) groups. Each of the hydroxyl groups can participate in hydrogen-bonding interactions with other molecules through its lone pair of electrons. The ability of glycerol to donate hydrogen bonds is thought to play a role in its ability to stabilize proteins and enzymes in solution, through the formation of hydrogen bonds between the glycerol and the amino acid residues in the proteins and enzymes.
A eutectic mixture is formed at a particular molar ratio which, in this case, has been observed at 1:10 at 60 °C when both components were stirred at 100 rpm until a homogenous, stable, and clear mixture was obtained. Table 4 shows the formulation of AA:Gly NADES.

### Table 4. Preparation of AA:Gly NADES.

<table>
<thead>
<tr>
<th>Molar Ratios (AA:Gly)</th>
<th>Observation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1, 1:2, 1:3, 1:4, 1:5</td>
<td>Cloudy and turbid</td>
</tr>
<tr>
<td>1:6, 1:7, 1:8, 1:9</td>
<td>Less cloudy but high precipitation</td>
</tr>
<tr>
<td>1:10</td>
<td>Transparent, clear and stable (Eutectic Mixture)</td>
</tr>
</tbody>
</table>

3.2. YP/PV of Mud Samples

Yield point (YP) refers to the attraction between particles of a colloidal in the drilling mud slurry, and plastic viscosity (PV) refers to the resistance offered by solid particles and the liquid in the drilling fluid [41]. The mud hydraulics and the ability to carry cuttings to the surface can be calculated by the ratio of YP to PV. Generally, a surge in YP/PV values improves the flow profile and the cutting/carrying ability of the mud. However, it is important to note that very high values of YP/PV can lead to an increase in annular frictional pressure losses and equivalent circulation density (ECD), potentially causing formation fractures. The literature suggests that YP/PV values in the range of 0.75–1 lbm/100 ft²/cp are ideal for good cutting transportation without causing unwarranted ECD [42,43]. The addition of DES in the mud improves the cutting carrying ability by decreasing the YP/PV value closer to the optimum range, this is due to the fact that, similar to ionic liquids, DESs alter the structure of clay platelets modifying the mud rheology. For aged samples, it can be seen that the YP/PV values are closer to the optimum range, as shown in Figure 1. As the temperature increases, the ratio of YP/PV in the drilling mud decreases due to a variety of factors such as changes in the electrical double-layer width around clay particles, a decrease in hydration, increased thermal energy of clay particles, and a decrease in the viscosity of the colloidal solution. At high temperatures, bentonite experiences significant dehydration, degradation, and mechanical shearing. This causes the clay platelets to come closer together, creating attractive forces between them that result in a face-to-edge orientation [44,45]. This rise in temperature leads to the state of agglomeration and flocculation that results in lower rheological properties. NADES shows optimum performance at 3%, where YP/PV values were closest to the optimum range. Figure 2 depicts the comparison of YP/PV values with other inhibitors, which proves all inhibitors have improved YP/PV values of the mud, though CC:Urea DES and AA:Gly NADES have shown the best results.

![Figure 1. YP/PV of AA:Gly NADES-based mud samples before and after aging.](image-url)
Ascorbic acid-based NADES performed exceptionally well under high-temperature, high-pressure conditions. Compared to the base sample, the addition of NADES not only reduced the thickness of the mud cake but also decreased the filtrate volume, as shown in Figures 3–5. Problems such as drill pipe sticking can occur when there is a thick mud cake, which is why thinner is added to the drilling mud to decrease its thickness. NADES in the mud acts as a thinner, reducing the thickness of the mud cake and filtrate volume. This is likely due to the NADES’ ability to interact with clay platelets and change their wettability, thus reducing the thickness of the mud cake. Using 3% NADES without aging resulted in a minimum mud cake thickness of 1.2 mm and 18 mL of filtrate loss, as shown in Figures 3 and 5. The addition of 3% NADES resulted in a 39.69% reduction in mud cake thickness and 28% reduction in filtrate volume compared to the base sample. When the aging temperature is increased, clay particles flocculate and aggregate, leading to a thicker mud cake and increased filtrate loss, as also shown in Figures 3 and 5. Figures 4 and 6 present a comparison of filtration properties of 3% AA:Gly NADES-based mud with other inhibitors. Among all inhibitors, NADES gave the best filtration properties, followed by CC:Urea DES, then, ionic liquids, and lastly, KCl. More discussion of the results is provided in Section 4. Moreover, error bars are drawn in Figures 3 and 5, based upon 5% error margin.
while the maximum recovery of 87% was observed when 3% NADES was utilized. The (with no NADES) results in 72% linear swelling. The addition of NADES in the mud samples, while the maximum recovery of 87% was obtained when 3% NADES was added to the drilling mud, resulting in only 16% swelling or 77.77% inhibition. Figure 8 illustrates the results for shale recovery. The presence of illite in the clay is mainly responsible for the dispersion of shale, leading to poor borehole cleaning and ineffective drilling. 12% shale recovery was observed with the base drilling mud samples, while the maximum recovery of 87% was observed when 3% NADES was utilized. The enhanced shale recovery can be linked to the incremented shale stabilization after the interaction of clay (in shale) with NADES in the drilling mud. The shale-swelling-inhibition

**3.4. Linear Swelling and Shale Recovery Tests**

The change in linear swelling for AA:Gly-NADES-based mud samples with different concentrations and KCl (5%), EMIMCl (3%), CC:Urea (3%)-based mud were evaluated and compared to the base drilling fluid sample. Figure 7 shows that the base sample (with no NADES) results in 72% linear swelling. The addition of NADES in the mud significantly reduced the linear swelling to 16% and the best results were obtained when 3% NADES was added to the drilling mud, resulting in only 16% swelling or 77.77% inhibition. Figure 8 illustrates the results for shale recovery. The presence of illite in the clay is mainly responsible for the dispersion of shale, leading to poor borehole cleaning and ineffective drilling. 12% shale recovery was observed with the base drilling mud samples, while the maximum recovery of 87% was observed when 3% NADES was utilized. The enhanced shale recovery can be linked to the incremented shale stabilization after the interaction of clay (in shale) with NADES in the drilling mud. The shale-swelling-inhibition

![Filtrate Volume Comparison](image1)

**Figure 4.** Comparison of filtrate volume of NADES-based mud with other inhibitors.

![Mudcake Thickness Comparison](image2)

**Figure 5.** Mud cake thickness of AA:Gly NADES-based mud.

![Mudcake Thickness](image3)

**Figure 6.** Comparison of mud cake thickness of NADES-based mud with other inhibitors.

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capability of NADES is linked to its excellent hydrogen-bond-formation capability with clay particles. NADES bonds with negatively charged clay granules and attaches onto the surface, thus neutralizing the negative charge on clay surface, and stabilizing the shale-hydration process. Furthermore, NADES also expels water between the hydrated clay layers, as confirmed from the results of d-spacing. Surface tension and Zeta potential results support the experimental results for linear swelling, which were discussed further.

Figure 7. Linear swelling of wafer caused by various inhibitors in drilling mud.

![Linear Swelling Graph](image)

Figure 8. Shale recovery caused by various inhibitors in drilling mud.

![Shale Recovery Graph](image)

3.5. D-Spacing of Inhibitors Based Mud

D-spacing is a measure of the combined length of the interlayer spacing of clay and one alumino-silicate layer within the clay [46]. Figure 9 presents the d-spacing results of dry Sodium Bentonite (Na-Bt), hydrated mud samples, and NADES-based mud samples. The results of d-spacing help in understanding the intercalation of water and NADES into clay layers. The d-spacing of dry Na-Bt increases with the addition of water, indicating that water has intercalated between the clay layers. However, the addition of NADES into the base mud decreases the d-spacing, showing that NADES has a higher affinity for clay than water and has expelled water out of the clay layers. The d-spacing of dry Na-Bt is found to be 12.64 Å, which increases to 18.01 Å after hydrating the Na-Bt.

![D-Spacing Graph](image)
3% and 5% NADES, 3% and 5% NADES resulted in the maximum elimination of water between the clay layers as shown by the maximum decline in d-spacing of 14.1 Å and 14 Å, respectively as shown in Figure 9. There is a slight difference in d-spacing of 5% NADES as compared to d-spacing of 3% NADES, indicating that the maximum intercalation of NADES into the clay layers can occur only till 5%. This decrease in d-spacing values depicts that the NADES (inhibitor) have efficiently intercalated between the clay layers and have excluded the water out from the clay layers. Other inhibitors such as KCl, EMIM-Cl and CC:Urea DES were also able to intercalate into clay layers and decrease the d-spacing as shown in Figure 9.

3.6. Surface Tension of Inhibitors Based Mud

Surface tension is the tension existing on the liquid surface due to the cohesive forces between the molecules of a liquid. Capillary pressure, also known as capillarity, is the pressure that arises in a liquid due to the adhesion of the liquid molecules to the surface of the container or the liquid-air interface [47,48]. The two are related because the capillary pressure is directly proportional to the surface tension of a liquid. The greater the surface tension, the greater the capillary pressure and vice versa. When the capillary pressure at the surface of shale/clay is higher, more water cations will be attracted to enter the clay layers, causing swelling. Shale inhibitors can reduce surface activity and decrease the surface tension, which hinders the invasion of water cations into the clay layers. The anti-swelling properties of clay can be understood by studying the surface tension of the base mud and NADES-based mud at various concentrations. The maximum decline of 31.74% in surface tension was observed for 3% NADES (inhibitor), while a 3% decline was observed for 5% KCl, as shown in Figure 10. The decrease in surface tension by NADES is due to its strong ability to form hydrogen bonds with clay, resulting in a change in the contact angle and capillary behavior, which, in turn, modifies the clay behavior in the presence of water. The results are consistent with the results of d-spacing and linear swelling. Figure 10 shows error bars that have been drawn based upon 5% error margin.
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The most significant reduction of 54.54% causes the maximum decline in Z.P., thus affecting the electrical double layer accordingly, as shown in Figure 11. It is also evident that the addition of NADES and other inhibitors, no matter the concentration, affects the electrokinetic potential of clay.

3.7. Zeta Potential of Inhibitors Based Mud

Zeta potential is a measure of the electrical potential at the interface between a solid and a liquid, which is an important parameter in understanding the stability of suspensions and the behavior of colloidal systems. It is related to the clay swelling because the zeta potential is directly linked to the charge on the clay particles. Clays are negatively charged particles and have a high zeta potential. When clay particles are in contact with water, the water molecules are attracted to the negatively charged clay particles and cause clay swelling. The zeta potential of clay particles is also affected by the presence of other ions in the drilling mud, such as cations of NADES, which can neutralize the negative charge on the clay particles and reduce the clay swelling.

The zeta potential and diffused double layer (DDL) are closely related because the zeta potential is affected by the charge on the clay particles and the DDL is affected by the amount of water molecules in the electrical double layer surrounding the clay particle. A more negative zeta potential indicates a greater charge on the clay particles, which results in a greater attraction of water molecules to the clay particles and, therefore, to a thicker DDL. A thicker DDL causes more hydration of the clay particles, which leads to a greater clay swelling. Now keeping this in mind, let us understand the effect of NADES on zeta potential of bentonite and modified bentonite samples.

Smectite and Illite clay possess a negatively charged surface, which is liable to attract water cations into the clay layers, thus causing swelling [48]. The results of Zeta potential depict the effect of inhibitors on the thickness of the electric double layer of the clay. Figure 11 shows that the inhibitors decrease the electrical double layer thickness, which affects the cationic exchange between the inhibitors and the clay. The most significant decline in ZP (as with surface tension and d-spacing) can be seen for 3% NADES, i.e., 55.54%. The most significant reduction of 54.54% causes the maximum decline in Z.P., thus affecting the electrical double layer accordingly, as shown in Figure 11. It is also evident that the addition of NADES and other inhibitors, no matter the concentration, affects the electrokinetic potential of clay.

Figure 10. Surface tension of inhibitors-based drilling mud samples.
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Figure 12. FESEM of modified bentonite wafers.

3.8. FESEM of Modified Bentonite Wafers

The effect of DES or NADES on the size of sodium bentonite particles can depend on the specific type of DES and the conditions under which it is added. Some studies have shown that the addition of certain types of DES can cause the particles of bentonite to aggregate and form larger particles, while other studies have shown that the addition of certain types of DES or NADES can lead to a decrease in the size of bentonite particles.

When a DES or NADES is added to a suspension of bentonite particles, it can change the surface charge of the particles, making them more attractive to one another and promoting the formation of larger clusters or flocs. The formation of these larger clusters can lead to a decrease in the overall size of the bentonite particles in the suspension. Additionally, DESs can also change the rheological properties of the mud by modifying the structure of clay platelets; this modification can cause the particles to clump together and form larger clusters. The average particle size of virgin and modified bentonite wafers has been estimated, and is vividly presented in Figure 12. The addition of inhibitors decreases the overall particle size, which is in accordance with the results of d-spacing.

Figure 11. Zeta Potential of inhibitors-based drilling mud samples.

-5% A.A:Gly NADES
-3% A.A:Gly NADES
-1% A.A:Gly NADES
3% CC:Urea
3% EMIM-Cl
5% KCl
Base sample

Zeta Potential (mV)
-35 -30 -25 -20 -15 -10 -5 0

Figure 12. FESEM of: (A) dry bentonite at 500 nm resolution, (B) hydrated sodium bentonite at 500 nm, (C) 5% KCl based sodium bentonite wafer at 500 nm, (D) 3% EMIMCl based wafer at 5 μm, (E) 3% CC:Urea based wafer at 1 μm, (F) 3% AA:Gly based wafer at 1 μm.
4. Discussion of Results

NADESs can inhibit shale swelling by interacting with the clay minerals that make up the shale. Shale swelling occurs when clay minerals, such as smectite, absorb water and expand, which can cause problems such as increased mud viscosity, reduced wellbore stability, and decreased hydrocarbon production [49]. One of the ways that DESs can inhibit shale swelling is by reducing the amount of water that the clay minerals can absorb [49]. The hydrogen-bond-acceptor (HBA) component of the NADES can interact with the clay minerals and reduce the amount of water that they can adsorb by forming hydrogen bonds with the water molecules. This can limit the amount of expansion that occurs in the clay minerals and reduce the overall swelling of the shale by stabilizing the overall negative charge on the clay.

Another way that NADESs can inhibit shale swelling is by interacting with the clay mineral surfaces and altering their chemical and physical properties [33,50]. The HBD component of the NADES can interact with the clay minerals and change their surface charge, which can affect the way that they interact with water and other fluids. This can also limit the amount of expansion that occurs in the clay minerals and reduce the overall swelling of the shale. It is worth noting that the ability of a specific NADES or DES to inhibit shale swelling will depend on the specific HBA and HBD components used, as well as the properties of the shale and the specific application. NADESs can improve the filtration properties of drilling mud by reducing the number of solid particles that are carried over by the mud. One of the ways that NADESs can improve the filtration properties of drilling mud is by reducing the amount of clay particles in the mud. The hydrogen-bond-acceptor (HBA) component of the DES can interact with the clay minerals in the mud and reduce their ability to absorb water, which can cause them to flocculate and settle out of the mud [51].

In drilling mud, reducing the surface tension of shale may improve shale inhibition by making it more difficult for water to penetrate the shale and cause it to swell. This can be achieved by using a drilling fluid that has a low surface tension and a high viscosity, which can help to reduce the amount of water that is absorbed by the shale. However, it is worth noting that shale inhibition also depends on many other factors, such as the type and properties of the clay minerals present in the shale, the chemistry of the drilling fluid, and the properties of the shale, such as porosity and permeability. Therefore, while reducing the surface tension can be one way to improve shale inhibition, it is not the only factor. It is also important to test the drilling fluid in the field and monitor the results to determine the actual shale inhibition.

5. Conclusions

1. An ascorbic acid and glycerine-based NADES was prepared at a 1:10 molar ratio at 60 °C and was utilized as a drilling fluid additive for clay stabilization. AA:Gly improved the drilling fluid (rheological and filtration properties), decreased the linear swelling of clay, and increased the percentage recovery of shale.

2. The efficiency of in-house prepared NADES was compared with conventional shale inhibitor (KCl) and the contemporary additives most utilized in drilling fluid by various research groups, i.e., EMIM-Cl-based ionic liquids and CC:Urea-based DES. The results show that NADES performed the best in improving drilling fluid properties and clay stabilization. The performance of AA:Gly NADES is comparable with CC:Urea DES, but NADES is cheaper and more environmentally friendly.

3. NADES stabilizes the negatively charged clay by making a hydrogen bond with it, which neutralizes it, thus making it more stable against hydration. NADES also improves the dispersion of shale during drilling, which causes a lot of problem, such as bit balling and slow drilling.

4. The results of the surface tension analysis show that NADES decreases the surface tension, which, in turn, decreases the capillary pressure, thus stopping imbibition of water into the shale layers. Moreover, NADES expels water out from the clay layers,
which is evidenced by the decrease in d-spacing results. NADES also decreases the DDL thickness of the clay, which, in turn, is depicted by the smaller zeta potential. All of these characterizations help to better elucidate the mechanism of shale inhibition by NADES.

5. Thus, AA:Gly-based NADES is recommended as a potential drilling fluid additive for clay stabilization and improving drilling fluid properties.

6. Way Forward

The engineered NADES-based mud will be a cheaper and greener alternative to traditional drilling fluid additives for improving drilling fluid properties, and thus, is recommended to the petroleum industry as a potential additive. In the future, various other combinations of NADESs can be exploited to determine their efficacy as drilling fluid additives.

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