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Eco-Friendly Drilling Fluid: Calcium Chloride-Based Natural Deep Eutectic Solvent (NADES) as an All-Rounder Additive

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Abstract: Designing an effective drilling mud is a critical aspect of the drilling process. A well-designed drilling mud should not only provide efficient mud hydraulics but also fulfill three important functions: enhancing mud rheology, inhibiting hydrate formation in deepwater drilling, and suppressing shale swelling when drilling through shale formations. Achieving these functions often requires the use of various additives, but these additives are often expensive, non-biodegradable, and have significant environmental impacts. To address these concerns, researchers have explored the potential applications of ionic liquids and deep eutectic solvents in drilling mud design, which have shown promising results. However, an even more environmentally friendly alternative has emerged in the form of natural deep eutectic solvents (NADES). This research focuses on an in-house-prepared NADES based on calcium chloride and glycerine, with a ratio of 1:4, prepared at 60 °C, and utilizes it as a drilling mud additive following the API 13 B-1 standards and checks its candidacy as a rheology modifier, hydrates, and shale inhibitor. The findings of the study demonstrate that the NADES-based mud significantly improves the overall yield point to plastic viscosity ratio (YP/PV) of the mud, provides good gel strength, and inhibits hydrate formation by up to 80%. Additionally, it has shown an impressive 62.8% inhibition of shale swelling while allowing for 84.1% improved shale recovery. Moreover, the NADES-based mud exhibits a 28% and 25% reduction in mud filtrate and mud cake thickness, respectively, which is further supported by the results of XRD, zeta potential, and surface tension. Based on these positive outcomes, the calcium chloride–glycerine NADES-based mud is recommended as a versatile drilling mud additive suitable for various industrial applications. Furthermore, it presents a more environmentally friendly option compared to traditional additives, addressing concerns about cost, biodegradability, and environmental impact in the drilling process for an ultimate global impact.

Keywords: NADES; shale swelling; drilling fluid; mud rheology; hydrate inhibition

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1. Introduction

Drilling mud, being a complex fluid system, often requires the incorporation of additives to enhance its performance and address specific challenges encountered during drilling operations [1]. These additives in general serve three major purposes: improving rheological properties, inhibiting hydrate formation during drilling, and suppressing shale swelling while drilling through shale rock [2]. However, it is important to consider the potential disadvantages associated with traditional additives, as well as explore alternative options that offer promising solutions. One of the major concerns with traditional drilling mud additives is their environmental impact [3]. Certain additives, such as synthetic polymers, can be detrimental to the environment. They may exhibit toxicity, lack biodegradability, or pose challenges in terms of treatment and disposal [4]. This raises concerns about potential contamination of soil and water resources, emphasizing the need for environmentally friendly alternatives. Another factor to consider is the cost of traditional additives. Some additives used in drilling mud formulations can be expensive, which can significantly impact drilling operations' overall cost [5]. This cost aspect necessitates exploring cost-effective alternatives that can maintain or improve drilling mud performance without straining the budget.

To address these concerns, researchers and industry professionals have been exploring the potential of innovative additives such as ionic liquids and deep eutectic solvents [6]. Ionic liquids are molten salts with unique properties, including low volatility, high thermal stability, and tunable chemical characteristics. These properties make them attractive candidates for various applications, including drilling mud formulations. Deep eutectic solvents, on the other hand, are a type of liquid mixture formed by combining a hydrogen bond donor and a hydrogen bond acceptor. These solvents exhibit characteristics such as low volatility, low toxicity, and biodegradability. They can be tailored to possess desired properties, making them a promising alternative to traditional drilling mud additives.

Various studies have demonstrated the efficacy of ionic liquids as shale inhibitors. In a study by Rahman et al. (2022), the use of tetramethylammonium chloride and 1-ethyl-3-methylimidazolium chloride in drilling mud resulted in a reduction of 23.40% and 15.66% in linear swelling, respectively [7]. Similarly, Rizwan et al. (2021) found that employing a trihexyltetradecyl phosphonium bis(2,4,4-trimethyl pentyl) phosphonate-based ionic liquid led to a 12.3% reduction in shale swelling compared to water [8,9]. Another study conducted by Huuang et al. (2020) revealed that the utilization of ionic liquids such as 1-hexyl-3-methylimidazolium bromide and 1,2-bis(3-hexylimidazolium1-yl) ethane bromide with Na-Bt pellets resulted in significant reductions of 86.43% and 94.17% in shale swelling, respectively [10]. Yang et al. (2019) employed 1-Vinyl-3-dodecylimidazolium bromide and 1-Vinyl-3-tetradecylimidazolium bromide, leading to reductions of 16.91% and 5.81% in shale swelling, respectively [11]. Ofei et al. (2017) utilized 1-butyl-3-methylimidazolium chloride (BMIM-Cl) in a water-based mud, observing up to a 50% decrease in mud cake thickness and a reduction in yield point/plastic viscosity (YP/PV) [12]. Furthermore, a study conducted by Yang et al. (2017) found that the use of 1-Vinyl-3-ethylimidazolium bromide resulted in a 31.62% reduction in shale swelling, accompanied by a shale recovery rate of 40.60%, as reported by Luo, Wang et al. (2017) [13]. In a study by Luo et al. (2017), the utilization of 1-octyl-3-methylimidazolium tetraflouroboreate resulted in an impressive 80% reduction in shale swelling [14].

In their study, Jia et al. (2019) investigated the use of deep eutectic solvents (DES) as shale inhibitors and observed significant inhibition of bentonite swelling. Different DES compositions, namely propanoic acid ChCl (1:1), 3-phenyl propanoic acid ChCl (1:2), and 3-mercapto propanoic acid + Itaconic acid + ChCl (1:1:2), demonstrated inhibition rates of 68%, 58%, and 58%, respectively [15]. Rasool et al. (2021) employed a glycerine/potassium carbonate DES (2:1) for swelling shale samples, achieving an impressive 87% inhibition of swelling [16,17]. Furthermore, Rasool et al. (2022) employed a combination of a potassium carbonate-based DES and poly (2-ethyl-2-Oxazoline) hydroxyl-terminated polymer as a double-action inhibitor in drilling mud, resulting in a remarkable 76% inhibition of swelling [18].

However, it is essential to acknowledge that even innovative additives such as ionic liquids and deep eutectic solvents have their own set of challenges [19]. Ionic liquids can sometimes have higher costs due to the complexity of their synthesis or purification processes. Additionally, the selection of the appropriate ionic liquid for a specific drilling mud application requires careful consideration of factors such as compatibility, stability, and environmental impact [20–22]. Similarly, the utilization of deep eutectic solvents as drilling mud additives may require further research and development and they are not green in a true sense as most of them utilize ammonium-based salts, which are not environmentally friendly [23]. The identification of suitable combinations of hydrogen bond donors and acceptors, as well as an in-depth understanding of their compatibility with other drilling mud components, is necessary. Additionally, a thorough evaluation of the performance and environmental impact of deep eutectic solvents is crucial before their widespread adoption.

In recent years, the potential of natural deep eutectic solvents (NADES) has emerged as an intriguing avenue for drilling mud additives and many other related applications in petroleum engineering [24]. NADES are derived from natural compounds, offering advantages such as biodegradability, lower production costs, and reduced environmental impact. The use of NADES as drilling mud additives holds promise for both enhanced performance and environmental sustainability. Utilizing natural deep eutectic solvents (NADES) as additives in drilling mud offers a multifaceted approach to enhance mud rheology, inhibit hydrate formation, and suppress shale swelling. NADES, derived from natural compounds, exert their effects through specific mechanisms.

For improving mud rheology, NADES act as rheology modifiers by adjusting viscosity, density, and gel strength [25,26]. The unique composition of NADES allows them to alter the flow properties of the drilling mud, enhancing its ability to carry and suspend solid particles, such as drill cuttings [6]. This optimization ensures the efficient removal of cuttings from the wellbore, reducing the risk of clogging and improving overall drilling performance. In terms of hydrate inhibition, NADES disrupt the conditions necessary for hydrate formation. The specific chemical properties of NADES, including their low freezing points and ability to interact with water molecules, hinder the formation of ice-like solids. By incorporating NADES into drilling mud, the risk of hydrate blockage is minimized, ensuring the uninterrupted flow of gas and preventing equipment damage [27]. NADES also exhibit shale inhibition properties by suppressing the swelling and disintegration of clay-rich shale formations. Through their chemical composition and interactions with shale particles, NADES reduce water absorption and minimize swelling. This stabilizes the shale formations and helps maintain wellbore integrity during drilling operations, mitigating the risks associated with wellbore instability and improving overall drilling efficiency [28].

By harnessing the unique mechanisms of NADES, drilling mud can benefit from improved mud rheology, enhanced hydrate inhibition, and effective suppression of shale swelling. The utilization of NADES as additives in drilling operations represents a promising approach for optimizing drilling performance while also emphasizing environmental sustainability through the use of natural compounds. Recently, an ascorbic acid-based NADES was utilized as a drilling mud additive for stabilization and had positive results [29]. NADES (natural deep eutectic solvents) offer a promising combination of biodegradability and cost-effectiveness, making them an attractive option in various applications. Their inherent biodegradability ensures that they can break down into environmentally benign components, minimizing potential ecological impacts. This characteristic aligns with sustainability goals and regulatory requirements. Additionally, NADES can be synthesized from readily available and economically viable components, making them a cost-effective alternative to traditional solvents [4,30]. Their sustainable nature and cost efficiency position NADES as a compelling choice for industries seeking environmentally friendly solutions without compromising on affordability.

The current research aims to explore the utilization of calcium chloride–glycerine-based natural deep eutectic solvents (NADES) as additives in mud. The motivation behind this study is to investigate the potential of these NADES in serving as effective rheology modifiers, hydrate inhibitors, and shale inhibitors. By incorporating these NADES into the mud, it is anticipated that their unique properties will contribute to enhancing the overall performance of the drilling mud. The rheological properties of the drilling mud can be optimized, ensuring efficient transport of drill cuttings and maintaining wellbore stability. Additionally, the potential of these NADES to inhibit hydrate formation will mitigate the risk of blockages and equipment damage, enabling a safe and uninterrupted flow of hydrocarbons. Furthermore, their ability to suppress shale swelling and improve shale recovery will also be evaluated. The current research will not only focus on the utilization of calcium chloride–glycerine-based natural deep eutectic solvents (NADES) as drilling mud additives but also involve comprehensive characterizations to provide a thorough understanding of their effects. Various characterization techniques, including X-ray diffraction (XRD), surface tension analysis, and zeta potential measurements, were used to elucidate the results and justify the underlying mechanism.

2. Materials and Methods

2.1. In-House Preparation of Calcium–Glycerine (CC:Gly) NADES Molar Ratios

The resulting mixture exhibited a transparent and uniform appearance, indicating the attainment of its eutectic composition. Experimental procedures involved the use of a METTLER Digital Balance for precise ingredient weighing and a Thermo Fisher Hot plate for controlled heating and stirring at a speed of 100 rpm. Additional characterization techniques, such as FTIR and NMR, will be conducted and the findings will be detailed in a subsequent publication.

Screening Criteria for Selecting HBD and HBA for NADES

The selection of hydrogen bond donor (HBD) and hydrogen bond acceptor (HBA) components for the natural deep eutectic solvents (NADES) screening criteria was based on prior research conducted by Rasool, Ahmad et al. (2022) [31]. This research demonstrated that components with a higher hydrogen bond count and polar functional groups exhibited greater effectiveness in shale inhibition.

2.2. Drilling Mud Preparation

The drilling mud was formulated in accordance with the API 13B-1 standard [32]. To prepare the mud, caustic soda (0.25 g) and sodium carbonate (0.25 g) were sourced from Sigma-Aldrich, Selangor, Malaysia. These ingredients, along with 22.5 g sodium bentonite (Na-Bt), were then combined with 350 mL of distilled water and thoroughly stirred in a multimixer for a duration of 40 min. Different concentrations of NADES (1%, 3%, and 5%) were added to the drilling fluid while mixing to optimize the hydrate inhibition and mud rheology results. The literature survey showed that various DES give optimum results at low concentrations, so we chose concentrations of 1–5% for this research work.

Drilling Mud Properties

Mud samples containing different concentrations of NADES were analyzed using a FANN Viscometer. Readings were recorded at speeds of 3 rpm, 6 rpm, 300 rpm, and 600 rpm, both before and after subjecting the samples to aging at temperatures of 100 °C and 150 °C. The aging process involved placing the mud samples in a rolling oven at a pressure of 1000 psia for a duration of 16 h. The obtained values were then used to calculate various parameters, including yield point (YP), plastic viscosity (PV), and 10 s and 10 min gel strength (G.S). The calculations were carried out according to API 13B-1 standards [32] and the corresponding Equations (1) and (2).

$$PV = \theta_{600} - \theta_{300} \tag{1}$$

$$YP = \theta_{300} - PV \tag{2}$$

The API 13B-1 guidelines [32] were followed to conduct an HPHT filtration test at a temperature of 150 °C and pressure of 400 psia. This test aimed to determine the amount of filtrate loss and the thickness of the mud cake in drilling mud samples. The testing equipment included a mud cell, which was pressurized using valve stems, and placed within a jacket that maintained a constant temperature through thermostatic control. The temperature was adjusted as required for the test. After pressurizing the cell, the filtrate volume and mud cake thickness were measured after a duration of 30 min. The obtained results are thoroughly analyzed in Section 3.

2.3. Shale Stabilization Studies

2.3.1. Bentonite Wafer Preparation

To investigate shale swelling, the research utilized bentonite wafers due to their composition containing the clay mineral smectite, which is responsible for shale swelling behavior. Acquiring authentic shale core samples is challenging since the coring process renders the shale unstable and often leads to the inclusion of other minerals such as sandstone and limestone. Conducting experiments on shale outcrops is not feasible as they typically lack smectite. In this study, Na-bentonite powder was compressed into pellets with a diameter of 2.54 cm and a weight of 11.5 g using a hydraulic press at a pressure of 1600 psi. The thickness of the pellets was measured prior to their placement in the linear swell meter (LSM) environment. Within the LSM, the pellets were submerged in drilling mud samples, including both the base sample and samples containing inhibitors. The LSM measured the change in thickness of the pellets at 60 s intervals for a duration of 24 h. The composition of sodium bentonite was determined using XRD, and Table 1 shows the percentage composition of bentonite.

Table 1. Percentage composition of sodium bentonite.

Mineral	Percentage
Quartz	29%
Hematite	4.7%
Carbonates	9%
Smectite	47%
Hatrurite	4%
Sodium Oxide	1.83%
Iron Silicates	2.17%

2.3.2. Linear Swell Meter

The Grace HPHT Linear Swell Meter (M4600) is a dedicated instrument utilized for measuring changes in sample thickness, enabling the evaluation of water-based drilling muds' effectiveness in preventing shale swelling. It comprises two main components: the wafer compactor and the linear swell meter (Model: M4600). Bentonite wafers were produced using the Grace core/wafer compactor, and the subsequent swelling tests were performed using the linear swell meter (LSM), which provides real-time data on the swelling phenomenon.

2.3.3. Shale Recovery Test

A shale sample was acquired from Niah, Miri District in Sarawak, Malaysia. To examine the clay composition and evaluate its suitability for dispersion and shale recovery experiments, the sample underwent X-ray diffraction (XRD) analysis. Among the clay minerals analyzed, illite accounts for 18% of the composition, making it a significant component. Kaolinite, on the other hand, makes up the largest portion, with a percentage of 31%. This suggests that the shale sample contains a substantial amount of kaolinite. Chlorite, another clay mineral, represents 22% of the composition, indicating its presence in notable proportions. Vermiculite, with a percentage of 10%, and mica, with 19%, also contribute to the overall clay mineral composition. These percentages provide insights into the relative abundance of each clay mineral in the shale sample and help in understanding its mineralogical characteristics.

The shale recovery test involved immersing shale cuttings in drilling mud and aging them for 24 h under 1000 psia at 150 °C before subjecting them to a series of sieves with different mesh sizes. The cuttings were then separated based on size, and the percentage recovery was calculated by calculating the non-dispersed cuttings that were able to pass through a particular sieve size. This test provides valuable information on the effectiveness of the drilling mud in controlling shale and its ability to remove cuttings during drilling operations.

2.4. Hydrate Inhibition Study

Nucleation, a highly intricate process involving numerous molecules, poses challenges for direct experimental observation. Although several methods exist for studying nucleation, the most dependable approach is the measurement of induction time, which combines nucleation theory with experimental observations. In this particular investigation, the inhibitory effects of different concentrations of deep eutectic solvents (DES) on hydrate formation were examined by adding them to the drilling mud.

To determine the induction time of various mud samples, micro-DSC (differential scanning calorimetry) was employed, which can be further studied in our previous work [27]. The samples were subjected to cooling within a temperature range of −20 °C to +20 °C, while maintaining a pressure of 114 bar and a cooling rate of 0.1 K/min. Methane gas was used to form SII-type hydrates. The resulting graph of heat flow versus time exhibited two distinct peaks for each sample. The smaller peak indicated the formation of hydrates, while the larger peak corresponded to ice formation. The onset time of hydrate formation was determined by analyzing the smaller peak. Interestingly, it was observed that at higher pressures (above 70 bar), hydrates formed prior to ice, while the reverse was true at lower pressures.

2.5. Characterization Techniques

2.5.1. Surface Tension

Surface tension is the term used to describe the tension present on the surface of a liquid, caused by cohesive forces. This tension influences the capillary action, which leads to the penetration of water cations into the micropores of shale. The degree of invasion is directly related to the surface tension. To measure the surface tension of different NADES-based mud samples with various concentrations (1%, 3%, and 5%), an interfacial tensiometer (IFT) was utilized.

2.5.2. D-Spacing

The d-spacing refers to the measurement of the distance between the layers of alumino-silicate within clay, plus the thickness of a single alumino-silicate layer. In order to investigate the incorporation of inhibitors into the layers of bentonite, an analysis using X-ray diffraction (XRD) was conducted. This analysis involved the examination of various samples, including dry sodium bentonite, base mud, and wet drilling mud samples. The wet drilling mud samples consisted of different concentrations (1%, 3%, and 5%) of CC:Gly-based NADES.

To obtain XRD peaks, a benchtop X-ray diffractometer (D2 phaser) was used. The diffractometer operated at a current of 40 mA and 45 kV, utilizing Cu-Kα radiation with a wavelength of 1.54059 Å. Once the XRD peaks were obtained for both the wet samples and dry Na-Bt, the d-spacing was calculated using Bragg's equation.

2.5.3. Zeta Potential Measurement

The zeta potential of mud samples containing various concentrations (1%, 3%, and 5%) of NADES was determined using a laser-based system known as the Malvern Zetasizer. The Malvern Zetasizer operates by subjecting suspended particles in the liquid to an electric field and measuring their velocity of motion. This measurement provides valuable information about the zeta potential of the particles. The obtained zeta potential data are analyzed and discussed in Section 3.

3. Results and Discussion

3.1. In-House Preparation of NADES

In this research, calcium chloride and glycerol were chosen as the components for the formation of NADES based on M.H. screening criteria. Calcium chloride, represented by the chemical formula $CaCl_2$, acts as a hydrogen bond acceptor in the NADES composition. It possesses two potential hydrogen bond acceptor sites, both located on chloride, allowing for hydrogen bonding interactions through the partial negative charge on the chlorine atom. Glycerol, also known as glycerine, is a widely used substance found in various products such as food, cosmetics, and pharmaceuticals. It functions as a hydrogen bond donor in the NADES formulation. Glycerol contains three potential hydrogen bond donor sites located on each of its hydroxyl (-OH) groups. These hydroxyl groups can engage in hydrogen bonding interactions through their respective lone pairs of electrons. The ability of glycerol to donate hydrogen bonds is significant in stabilizing proteins and enzymes in solution, as it forms hydrogen bonds with the amino acid residues present in proteins and enzymes [33].

A eutectic mixture was achieved at a molar ratio of 1:4 at a temperature of 60 °C while stirring the components at 100 rpm. The stirring process continued until a homogeneous, stable, and clear mixture was obtained. The composition of the CC:Gly NADES formulation is presented in Table 2 and Figure 1.

Table 2. Synthesis of CC:Gly NADES with different molar ratios at 60 °C.

Molar Ratio	Observation
1:1	Cloudy and turbid
1:2	Turbid with ppt
1:3	Precipitated
1:4	Transparent, no precipitate (eutectic mixture)
2:1	Cloudy
2:2	Intensely cloudy

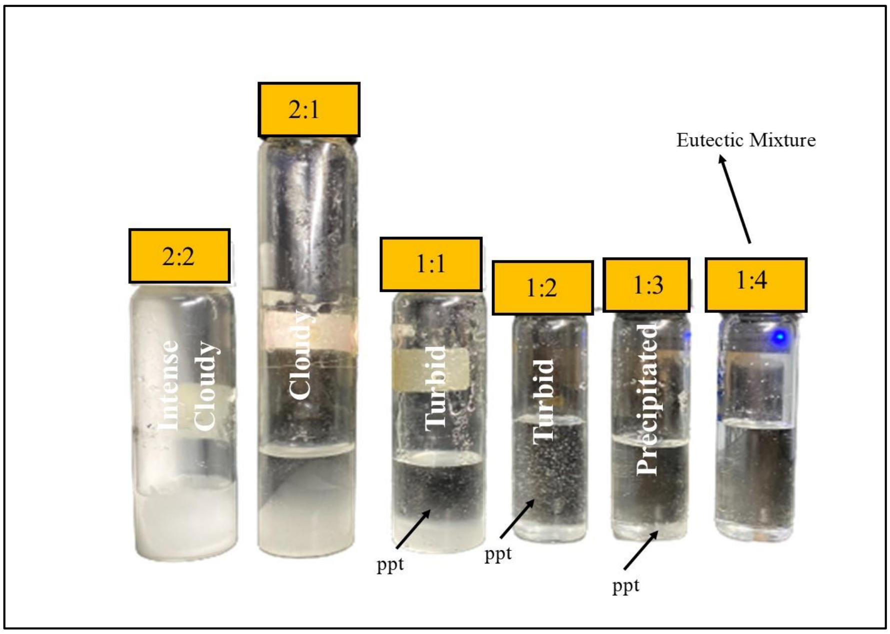

Figure 1. Preparation of calcium chloride–glycerine-based NADES with different molar ratios.

3.2. YP/PV of Mud Samples

The yield point (YP) is a parameter that measures the strength of the attractive forces between particles in a colloidal drilling mud slurry. Plastic viscosity (PV) quantifies the resistance offered by the solid particles and the liquid in the drilling mud. The ability of the mud to effectively transport cuttings to the surface depends on the ratio of YP to PV. Generally, increasing YP/PV values enhance the flow profile and cutting carrying capacity of the mud. However, excessively high values can lead to elevated annular frictional pressure losses and equivalent circulation density (ECD), potentially causing fractures in the formation. Existing literature suggests that YP/PV values within the range of 0.75–1 lbm/100 ft2/cp are optimal for efficient cutting transportation without undesired ECD effects.

The incorporation of deep eutectic solvents (NADES) into the mud helps improve the cutting carrying ability by reducing the YP/PV value closer to the ideal range. Similar to ionic liquids, NADES has the ability to modify the rheology of the mud by altering the structure of clay platelets. The YP/PV values of aged mud samples tend to approach the optimum range, as demonstrated in Figure 2. As temperature increases, the YP/PV ratio in the drilling mud decreases due to various factors. These factors include changes in the width of the electrical double layer around clay particles, reduced hydration, increased thermal energy of clay particles, and decreased viscosity of the colloidal solution. At higher temperatures, bentonite undergoes substantial dehydration, degradation, and mechanical shearing, causing the clay platelets to come closer together and resulting in increased attractive forces between them. This phenomenon affects the YP/PV ratio.

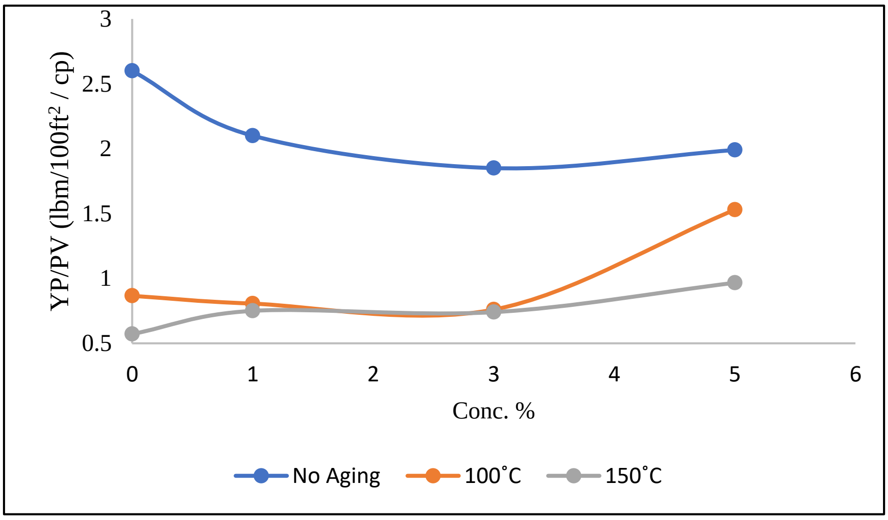

Figure 2. YP/PV of CC:Gly-based mud of aged and non-aged mud samples.

3.3. Filtration Properties of Mud

The performance of natural deep eutectic solvents (NADES) based on calcium chloride was remarkable, particularly under challenging conditions of high temperature and high pressure. The incorporation of NADES into the base drilling mud sample had dual benefits: it effectively reduced both the thickness of the mud cake and the volume of filtrate, as clearly depicted in Figures 3 and 4. Thick mud cakes have the potential to cause drill pipe sticking, which is why it is necessary to add substances that can make the mud thinner. NADES acts as a thinning agent by altering the wettability of clay platelets through interactive processes, thereby resulting in decreased mud cake thickness and filtrate volume. When 3% NADES was used without aging, the mud cake thickness was measured at 1.5 mm, and the filtrate loss was recorded as 18 mL, as demonstrated in Figures 3 and 4. Comparatively, the addition of 3% NADES led to a significant reduction of 25% in mud cake thickness and a 28% reduction in filtrate volume when compared to the base sample.

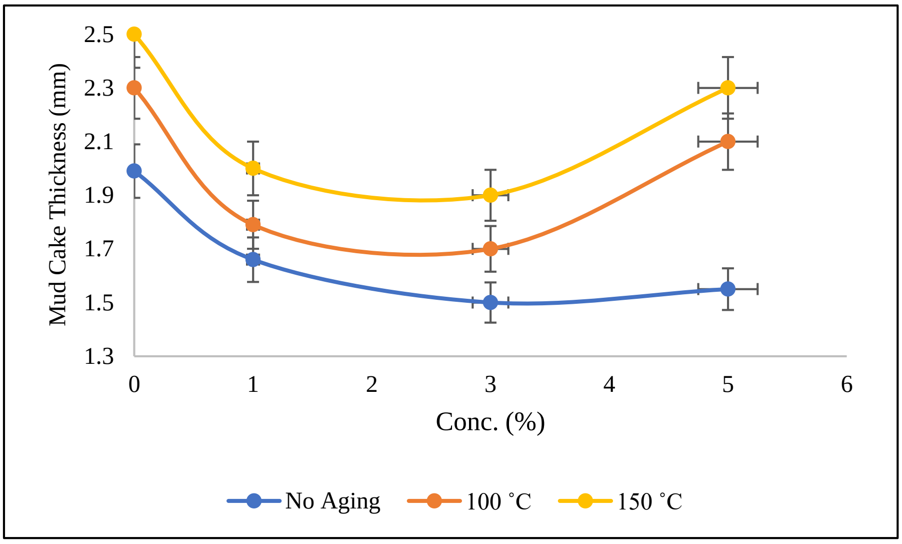

Figure 3. Mud cake thickness of CC:Gly-based mud for aged and non-aged mud samples.

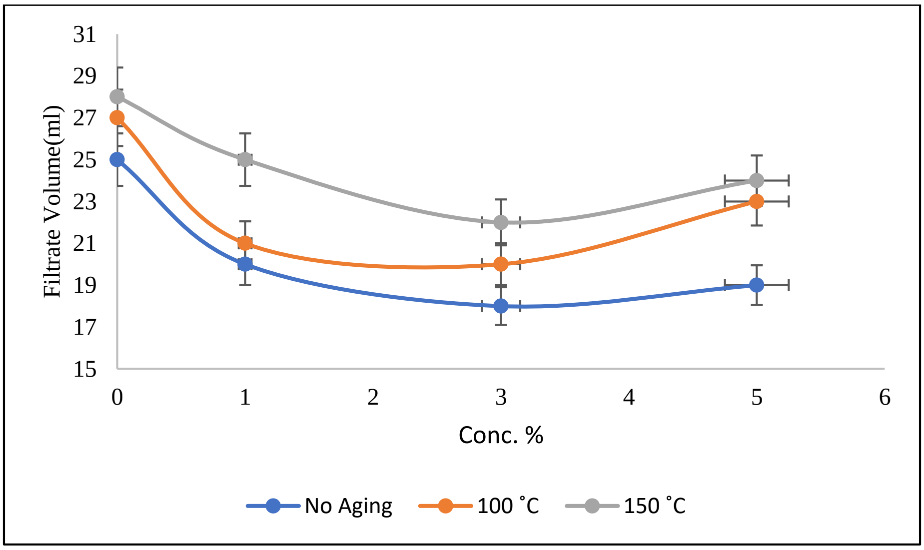

Figure 4. Filtrate volume of CC:Gly-based mudn for aged and non-aged mud samples.

It is important to note that as the aging temperature increases, the clay particles tend to flocculate and aggregate, leading to the formation of thicker mud cakes and increased filtrate loss, as illustrated in Figures 3 and 4. Error bars were drawn in Figures 3 and 4 to indicate 5% error margins.

3.4. Gel Strength

Gel strength refers to the mud's ability to retain suspended cuttings under static conditions. It is measured at three different time intervals: 10 s, 10 min, and 30 min. Although both gel strength and yield point are measured in the same units (lb/100 ft^2), yield point is a dynamic property, while gel strength can be considered a static property of the drilling mud. Gel strength is calculated by comparing the increase in gel strength from the previous reading at various time intervals. The larger the difference between readings, the higher the pump pressure needed to disrupt the gel and initiate circulation. In some cases, the mud may solidify, necessitating the addition of different chemicals to dilute it.

Examining Figure 5, it is apparent that the addition of NADES to the drilling mud did not significantly increase the gel strength. This observation holds true for both fresh and aged samples. All samples containing DES exhibited a hindrance in the increase in gel strength to a notable extent. However, the samples containing 3% NADES displayed the most substantial decline in the increment in gel strength.

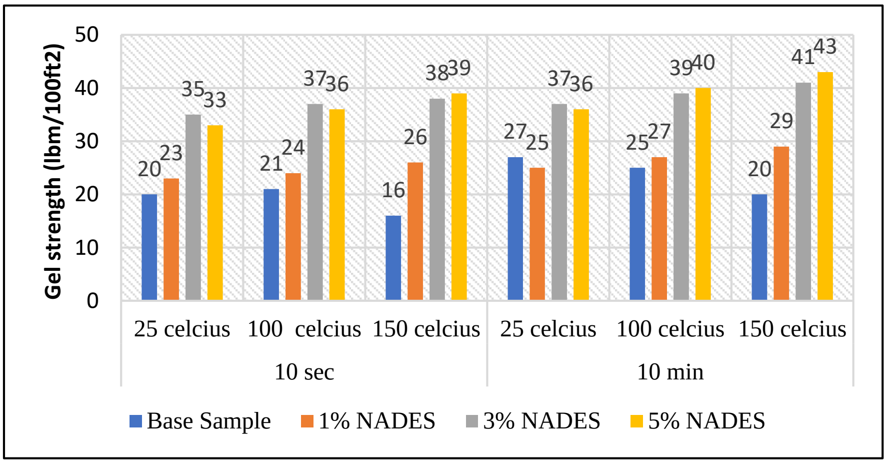

Figure 5. Gel strength of CC:Gly-based mud.

3.5. Induction Time of Hydrate Formation

The data presented in Table 3 and Figures 6 and 7 clearly indicate that the base sample effectively prevented hydrate formation for a duration of 4.185 h. Notably, when the mud contained NADES, the formation of hydrates was delayed even further, reaching a time of 6.523 h with the addition of 1% NADES. It is noteworthy that the inclusion of 3% NADES yielded the most favorable results (80% hydrate inhibition) in terms of inhibiting hydrate formation, while 5% NADES also gave close results. Further discussion of the results is given in Section 3.10.

Table 3. Hydrate and ICE onset times of NADES-based mud.

Conc.	Induction Time (h)	Peak Height (Hydrates) (mW)	Ice Onset Time (h)	Hydrate Onset Temperature (°C)
Base	4.185	7.948	5.439	−4.136
1%	6.523	7.284	6.214	−12.525
3%	7.573	12.715	6.361	−13.393
5%	7.213	80.97	6.42	−9.631

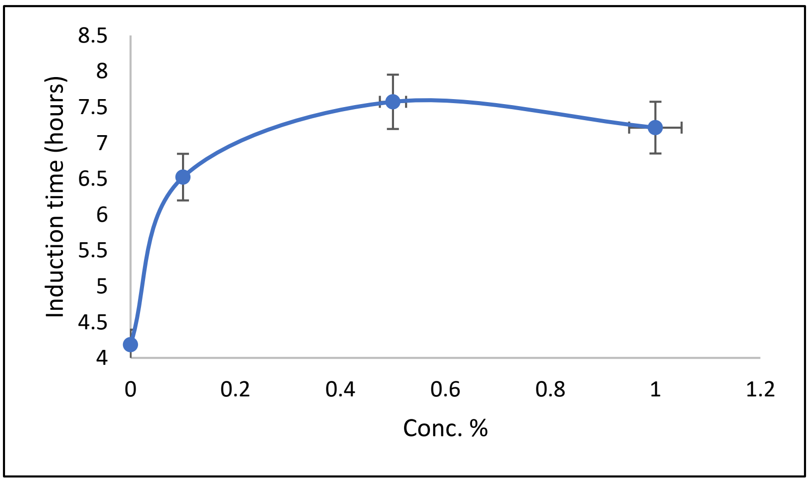

Figure 6. Hydrate induction time of CC:Gly-based mud.

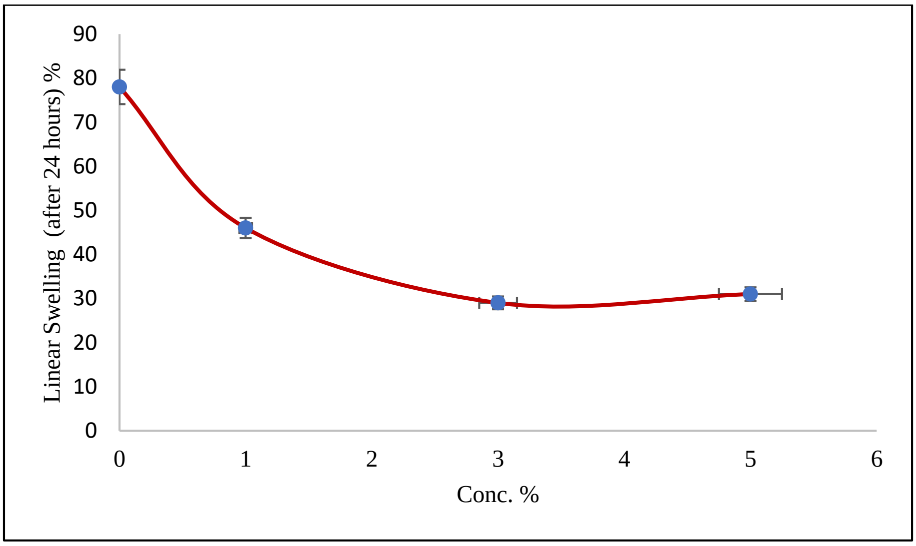

Figure 7. Linear swelling of CC:Gly-modified bentonite wafers.

3.6. Linear Swelling and Shale Recovery Tests (Dispersion Test)

The assessment of linear swelling was conducted to compare the effects of different concentrations of CC:Gly NADES-based mud samples with varying concentrations against the base drilling mud sample. Figure 7 visually represents the findings, demonstrating that the base sample without NADES exhibited a linear swelling of 78%. However, the addition of NADES significantly reduced the swelling to 29%, with the most favorable outcomes observed when 3% NADES was incorporated into the drilling mud. This concentration resulted in a mere 29% swelling or 62.8% inhibition.

Figure 8 presents the results of shale recovery, showing a 12% recovery rate for the base drilling mud and a remarkable 76% recovery rate when 3% NADES was employed. The improved shale recovery can be attributed to the stabilizing effect of NADES on the clay present in shale, which occurs through its interaction with the drilling mud. NADES forms bonds with the negatively charged clay particles, neutralizing the negative charge on the clay surface and thereby stabilizing the hydration process of shale. This capability is attributed to NADES' remarkable ability to form hydrogen bonds with clay particles. The experimental results for linear swelling find support in the analysis of d-spacing, which is further elaborated on in Section 3.7.

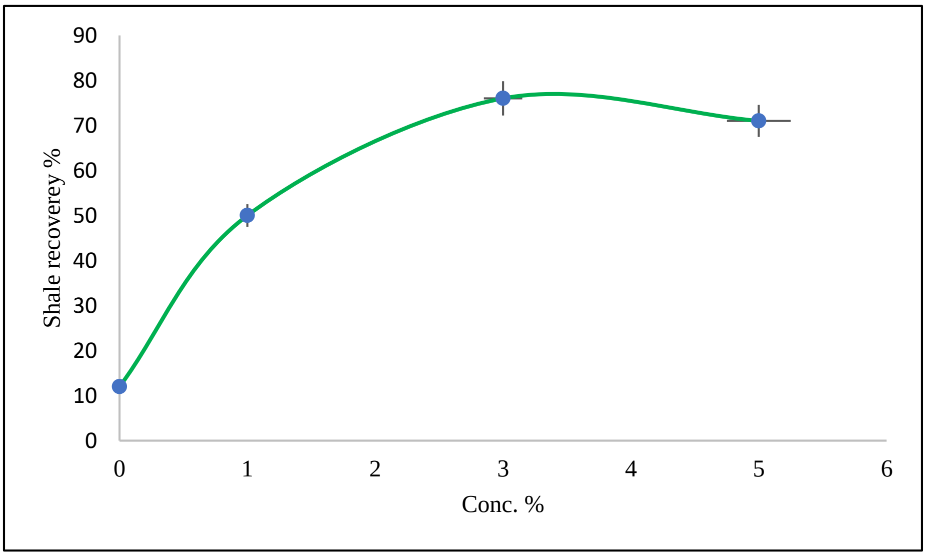

Figure 8. Shale recovery of CC:Gly-based mud.

3.7. D-Spacing of Inhibitor-Based Mud

D-spacing measures the combined length of the interlayer spacing of clay and one alumino-silicate layer within the clay. Figure 9 presents the d-spacing results for dry sodium bentonite (Na-Bt), hydrated mud samples, and NADES-based mud samples. The results help understand the intercalation of water and NADES into clay layers, with the d-spacing of dry Na-Bt increasing with the addition of water and decreasing with the addition of NADES, showing that NADES has a higher affinity for clay than water and expels water from the clay layers. The d-spacing of dry Na-Bt is 12.64 A^{o}, increasing to 18.01 A^{o} after hydration. The maximum elimination of water between the clay layers was observed with 3% and 5% NADES, resulting in a maximum decline in d-spacing of 14.23 A^{o} and 14.99 A^{o}, respectively, as shown in Figure 9.

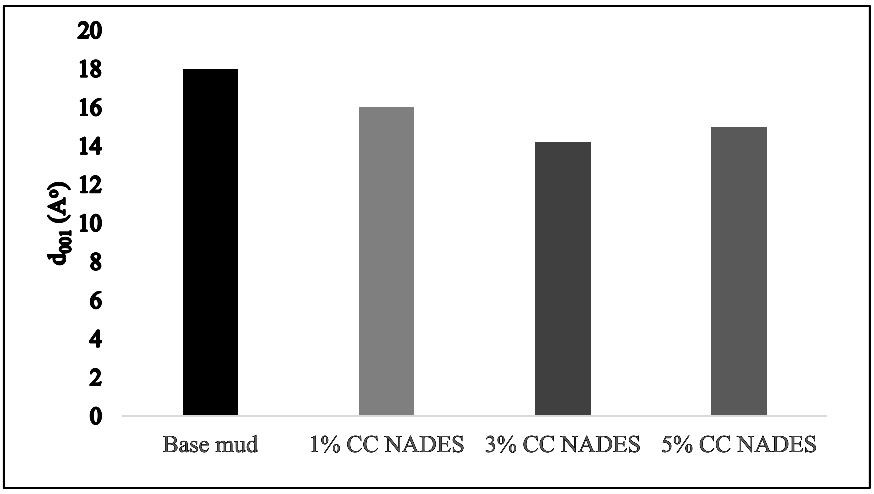

Figure 9. D-spacing of CC:Gly-based mud wafer.

3.8. Surface Tension

Surface tension, which refers to the cohesive forces between molecules at the surface of a liquid, plays a significant role in capillary pressure. Capillary pressure is the pressure exerted by a liquid as a result of the adhesion of its molecules to the container or air–liquid interface. The relationship between surface tension and capillary pressure is direct, meaning that higher surface tension results in higher capillary pressure. When it comes to shale inhibition, substances such as NADES can effectively reduce surface tension, preventing water cations from penetrating the layers of clay and thus mitigating shale swelling. The findings of surface tension testing revealed a significant decrease of up to 11.29% when 3% NADES was employed as shown in Figure 10. This decline can be attributed to the ability of NADES to form hydrogen bonds with clay, consequently altering its contact angle and behavior when exposed to water.

3.9. Zeta Potential

Zeta potential, which refers to the electrical potential at the interface between a solid and a liquid, plays a vital role in understanding the stability of suspensions and the behavior of colloidal systems [34]. In the context of clay swelling, zeta potential is closely related, as the negative charge present on clay particles attracts water molecules and promotes swelling [35]. However, the introduction of NADES can counterbalance this negative charge on the clay particles, leading to a reduction in swelling [9]. The results obtained from zeta potential testing demonstrated a significant decrease, with the most notable decline of 57.14% observed when using 5% NADES, which is closer to the Z.P of the 3% NADES-based sample as shown in Figure 11. This decline in zeta potential impacts the electrical double layer surrounding the clay particles, further influencing their behavior and stability.

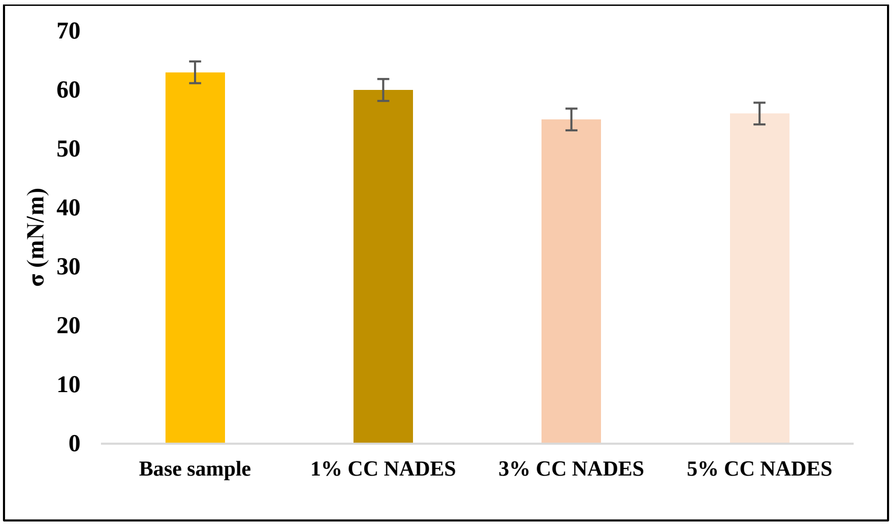

Figure 10. Surface tension of CC:Gly-based mud.

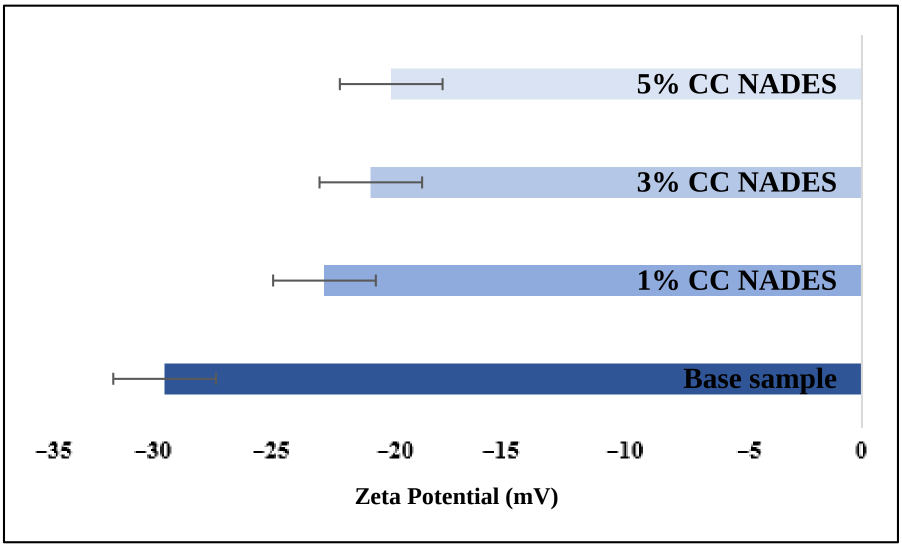

Figure 11. Zeta potential of CC:Gly-based mud.

In this research, calcium chloride and glycerol were chosen as the components for the formation of NADES based on M.H. screening criteria. Calcium chloride, represented by the chemical formula $CaCl_2$, acts as a hydrogen bond acceptor in the NADES composition. It possesses two potential hydrogen bond acceptor sites, with both located on chloride, allowing for hydrogen bonding interactions through the partial negative charge on the chlorine atom. Glycerol, also known as glycerine, is a widely used substance found in various products such as food, cosmetics, and pharmaceuticals. It functions as a hydrogen bond donor in the NADES formulation. Glycerol contains three potential hydrogen bond donor sites located on each of its hydroxyl (-OH) groups. These hydroxyl groups can engage in hydrogen bonding interactions through their respective lone pairs of electrons. The ability of glycerol to donate hydrogen bonds is significant in stabilizing proteins and enzymes in solution, as it forms hydrogen bonds with the amino acid residues present in proteins and enzymes [33].

3.10. Discussion on Underlying Mechanism

One of the key mechanisms through which NADES (natural deep eutectic solvents) can improve mud rheology is by influencing the face-to-edge orientation of bentonite particles.

Bentonite, a common clay mineral used in drilling mud, consists of thin, plate-like particles. These particles have a natural tendency to orient themselves with their faces parallel to each other, forming stacked layers. This face-to-face orientation leads to an increase in the mud viscosity and gel strength [36]. However, the addition of NADES to the drilling mud can modify this face-to-edge orientation of bentonite particles. NADES molecules have unique properties that can disrupt the face-to-face alignment of the bentonite particles. The NADES molecules penetrate the interlayer spaces of the bentonite, causing a reorientation of the particles from face to edge. This reorientation results in a more open and dispersed structure, reducing the viscosity and gel strength of the mud.

The mechanism behind NADES' ability to inhibit hydrate formation during drilling involves several factors, including induction time and nucleation inhibition. Induction time refers to the period required for the formation of the first hydrate crystals from the supersaturated drilling mud [37]. NADES can extend the induction time significantly, thereby delaying the onset of hydrate formation. This delay occurs due to the unique solvent properties of NADES, which interfere with the formation of hydrate crystal structures by making a hydrogen bond with it. NADES molecules have the ability to penetrate the water cages that form around gas molecules, disrupting the hydrogen bonding network necessary for hydrate formation. By occupying the spaces within the water cages, NADES hinder the efficient organization of water molecules into the stable hydrate lattice structure, which increases induction time and suppresses the growth of hydrates. Consequently, the formation of hydrate crystals is delayed, and the induction time is extended.

Furthermore, NADES can also inhibit nucleation, which is the initial step of hydrate formation when small clusters of hydrate molecules form and serve as the building blocks for larger crystals. NADES molecules act as inhibitors, preventing the clustering and growth of these hydrate nuclei. They achieve this by creating a physical barrier or steric hindrance that inhibits the aggregation of hydrate molecules and hinders the nucleation process. Moreover, the presence of NADES in the drilling mud alters the thermodynamic conditions required for hydrate formation. NADES can modify the water activity and salinity of the fluid, thereby shifting the hydrate formation conditions to less favorable regions of the phase diagram. This modification reduces the likelihood of hydrate formation and further contributes to hydrate inhibition [38].

NADES have the capability to prevent shale swelling by interacting with the clay minerals present in shale formations. Shale swelling occurs when clay minerals, such as smectite, absorb water and expand, leading to issues such as increased mud viscosity, compromised wellbore stability, and decreased hydrocarbon production [39]. The prevention of shale swelling by NADES is achieved through two main mechanisms. Firstly, NADES reduce the water absorption capacity of clay minerals by interacting with them through their hydrogen bond acceptor (HBA) component. This interaction forms hydrogen bonds with water molecules, thereby limiting the expansion of clay minerals and reducing overall shale swelling [40].

Additionally, NADES can prevent shale swelling by modifying the chemical and physical properties of clay mineral surfaces through their interaction with the hydrogen bond donor (HBD) component. This alteration of the surface charge of clay minerals affects their interaction with water and other fluids, thereby limiting their expansion and reducing shale swelling. The effectiveness of NADES or deep eutectic solvents (DES) in preventing shale swelling depends on various factors such as the specific HBA and HBD components used, the properties of the shale, and the particular application [41].

Moreover, NADES can enhance the filtration properties of drilling mud by reducing the presence of solid particles carried over by the mud. This is accomplished by the interaction of the HBA component with clay minerals, causing them to flocculate and settle out of the mud. It is important to note that while reducing surface tension through the use of drilling mud with low surface tension and high viscosity can improve shale inhibition, other factors such as clay mineral properties, drilling mud chemistry, and shale characteristics also play significant roles in shale inhibition. Therefore, it is crucial to conduct field testing and monitor the results to assess the effectiveness of the drilling mud in achieving shale inhibition may be divided by subheadings. This should provide a concise and precise description of the experimental results, their interpretation, as well as the experimental conclusions that can be drawn.

4. Conclusions

This study demonstrated that the NADES-based mud effectively improved mud rheology, inhibited hydrate formation, and suppressed shale swelling. The incorporation of NADES into the drilling mud led to significant enhancements in the mud's yield point to plastic viscosity ratio (YP/PV) and gel strength. This improvement in rheological properties contributes to better mud hydraulics and the ability to suspend cuttings in static conditions. Furthermore, the NADES formulation exhibited exceptional performance in inhibiting hydrate formation during drilling operations. By extending the induction time and impeding nucleation, the NADES significantly delayed the formation of hydrate crystals. This inhibitory effect can be attributed to the NADES' unique solvent properties, which disrupt the hydrogen bonding network necessary for hydrate formation. Moreover, the study revealed that the NADES-based mud effectively prevented shale swelling. By interacting with clay minerals present in shale formations, the NADES reduced water absorption and limited the expansion of clay minerals. This mitigated shale swelling, thereby ensuring improved wellbore stability, reduced mud viscosity, and enhanced hydrocarbon production.

In a nutshell, the results of the study indicate that the NADES-based mud offers significant improvements in the ratio of yield point to plastic viscosity (YP/PV) of the mud, as well as favorable gel strength and a remarkable 80% inhibition of hydrate formation. Moreover, it exhibits an impressive 62.8% reduction in shale swelling while enabling an 84.1% improvement in shale recovery. Additionally, the NADES-based mud demonstrates a notable decrease of 28% in mud filtrate and 25% in mud cake thickness, which is supported by the results obtained from XRD, zeta potential, and surface tension analyses. Based on these promising findings, the calcium chloride–glycerine NADES-based mud is recommended as a versatile additive for drilling mud, suitable for various industrial applications. Furthermore, this alternative presents a more environmentally friendly option compared to traditional additives, effectively addressing concerns related to cost, biodegradability, and environmental impact in the drilling process. Its potential for global impact cannot be overlooked, making it a valuable addition to the field of drilling operations.

Propelling Forward: It is recommended to conduct a detailed assessment for the comparison and compatibility of the combined effects of NADES and conventional additives on key drilling mud properties such as fluid loss control, shale inhibition, lubricity, rheological behavior, and thermal stability. This evaluation will help quantify the synergistic benefits and optimize the formulation for improved drilling performance.

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