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Evaluation of the Inhibition Performance of a Hybrid Depth Eutectic Solvent Used as an Inhibitor for Water-Based Drilling Fluids and Its Mechanistic Analysis

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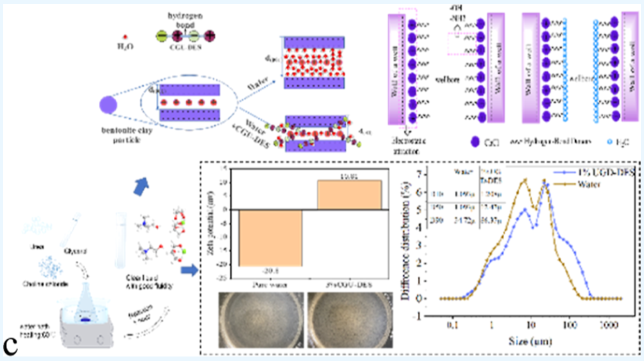

ABSTRACT: Drilling instability in oil and gas drilling has long challenged drilling safety and economics. Conventional oil-based drilling fluids offer high-temperature resistance and good inhibition. However, oil-based drilling fluids have significant problems in terms of environmental impact, cost, and waste fluid disposal. This has led to the widespread use of water-based drilling fluids. This study aims to investigate the synthesis of a new water-based drilling fluid inhibitor, a hybrid low eutectic solvent ChCl-Gly-Urea (CGU-DES), and its performance evaluation. While conventional eutectic solvents (DES) usually consist of a single type of hydrogen bond acceptor (HBA) and hydrogen bond donor (HBD), CGU-DES extends its performance characteristics by introducing a combination of one HBA and two HBDs. The study confirmed the successful synthesis of CGU-DES using FT-IR spectroscopy. The following advantages of CGU-DES over CU-DES and CU-DES consisting of a single type of HBA and HBD were verified. Below 175 °C, the temperature resistance of CGU-DES is better, and the mass loss rate is less than 5%. The first and second rolling recoveries of CGU-DES aqueous solution with low concentration (<0.5 wt %) were greater than 95% and 85%, respectively, higher than the rolling recoveries of CG-DES and CU-DES.CGU-DES has a good ability to reduce water activity. When the dosage is 10%, the activity of DES aqueous solution is less than 0.950, and the efficiency of reducing water activity is nearly twice that of CG-DES and CU-DES. CGU-DES is compatible with sodium slurry and drilling fluids with polymer-sulfonated materials because it has little influence on rheology and fluid loss. At 180 °C, 0.7% CGU-DES was added to the polysulfonate drilling fluid system, and the fluid loss reduction rate reached 30.59%. Experiments show that CGU-DES can inhibit the hydration and dispersion of shale by inserting into the crystal spacing of montmorillonite , adsorbing onto the surface, reducing the surface tension of drilling fluid, reducing the contact angle between drilling fluid and shale, and reducing the water activity of drilling fluid. In summary, CGU-DES, a new type of green solvent, has potential application prospects in water-based drilling fluids and provides new technical support for solving the borehole instability problem during drilling.

1. INTRODUCTION

It is well-known that wellbore instability in oil and gas drilling has always been an important subject. For a long time, this problem has seriously threatened the safety and economy of drilling projects.[1,2] Oil-based drilling fluid systems have the characteristics of high-temperature resistance and good inhibition; however, the environment, cost, and waste liquid disposal pose challenges to the use of oil-based mud.[3,4] To consider economic and environmental protection, water-based drilling fluids are often used in drilling fluids.[5] However, water molecules in water-based drilling fluids can lead to the hydration of clay minerals in shale formations, causing wellbore instability. Therefore, suitable inhibitive inhibitors in drilling fluid are crucial.[6]

Inhibitors are classified into traditional shale inhibitors, polyamine inhibitors, nanomaterials inhibitors, and other novel shale inhibitors.[7] Traditional shale inhibitors mostly use inorganic salts, such as potassium chloride and ammonium chloride. Potassium ion water-based drilling fluids are toxic to marine organisms, and the suitability of ammonium ion and anionic treatment agents is poor. As a kind of polymer, polyamine inhibitors have limitations in high-temperature

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drilling; their temperature resistance is poor; they are easy to decompose at high temperatures; and they have specific pH requirements. Nanomaterials have problems, with high prices and poor compatibility. Ionic liquid inhibitors in other novel treatment agents have good inhibition and thermal stability, but ionic liquids based on imidazoles are expensive, dangerous, and indecomposable.[8]

In other new shale inhibitors, low eutectic solvents (depth eutectic solvent (DES)) are increasingly concerned because they have the advantages of traditional ionic liquids but also offer lower cost, more straightforward preparation, biodegradability, biocompatibility, and nontoxic and harmless green characteristics, which is in line with China's green drilling development concept. These advantages also make DES widely studied in many research fields.[9,10] For example, its application areas include extraction,[11] biodiesel production,[12] biotechnology,[13] catalysis,[14] agri-food,[15] and polymer chemistry.[16] DES has numerous classifications,[17] while DESs contain large asymmetric ions with low lattice energy and melting points. They are usually obtained by a complex of quaternary ammonium salts with metal salts or hydrogen bond donors (HBDs). The charge separation of halogenated ions and HBD molecules through hydrogen bonds is such that the melting point of the mixture is lower relative to the melting point of the mixture than the melting point of the individual components.[18] From the molecular dynamics perspective, it is expressed that adding HBDs destroys the long-range ordering between cationic anions in choline chloride, significantly reducing the interaction energy between DES components.[19,20] The type III eutectic, which is formed by choline chloride and a HBD, is simple to prepare and has relatively little reaction with water. Many are biodegradable and cost relatively little. Because HBD dramatically impacts the physical properties of DES, there are many types of HBD of this type of DES, which means that the properties of this type of DES can be adjusted in a wide range, so it is suitable for research and application.[21]

DES usually refers to a mixture of two or more compounds.[22] Ma J[23] synthesized four low eutectic solvents (Urea-DES, Gly-DES, Oxa-DES, and Cite-DES) based on choline chloride, and the four DESs were effective in inhibiting shale hydration and swelling compared with conventional inhibitors such as potassium chloride (KCl) and polyetheramine. When the sodium bentonite (Na-bent) content is very high, the addition of 5% DESs can still maintain a low rheological parameter, and the addition of DESs does not affect the basic performance of drilling fluids. Ao H[24] prepared four kinds of DESs with different alkyl chain lengths that can effectively prevent shale hydration and swelling, and the DESs can be adsorbed on the surface of the clay through electrostatic attraction and hydrogen bonding. The hydration of clay is inhibited by compressing the electrical double layer. In addition, as DESs can enter the clay layer, they reduce the spacing of the clay layer, which reduces the osmotic hydration.

In 2022, Rasool's[25] study formulated a dual action P-D (polymer-deep eutectic solvent) inhibitor using a combination of potassium carbonate-based DES and modified oxazolidine-based polymers, which showed 76% inhibition with a maximum reduction in surface tension and zeta potential of 36% and 73%, respectively. In 2023, Rasool's[26] study used homemade ascorbic acid and glycerol (AA: Gly)-based NADES as a drilling fluid inhibitor, 3% NADES mud cake thickness was reduced by 39.69%, drilling fluid filtrate volume was reduced by 28%, and shale inhibition was achieved by 77.77% with shale recovery of 87%. In 2024, Rasool[27] prepared NADES in a molar ratio of 1:8 at 60 °C, and the addition of 3% NADES resulted in a 14.2% reduction in filtrate volume and a 19.2% reduction in cake thickness. In addition, 3% NADES inhibited clay swelling by 69.23% and shale recovery by 58%. Compared with 3% KCl and 3% 1-ethyl-3-methylimidazolium chloride (EMIM-Cl), the effect of NADES-based mud was superior to those of both.

As mentioned above, only a single type of hydrogen bond acceptor (HBA) and hydrogen bond donor (HBD) are discussed in most of the articles, while the literature on hybrid DES is very scarce. If a complex DES is composed of multiple types of HBA and HBD, then the DES properties can be extended by HBA: HBD combinations with different molecular functionalities. Multiple HBAs: HBD DES are regarded as mixtures of DES, and the significant deviation from the ideal condition is analyzed according to the thermal physical properties of the mixture. Thus, this situation suggests that multi-HBA: HBD DESs (hybrid DESs) have certain properties that belong to a single DES component, and there are additional effects that are not present in simple cases of DESs.[28,29] Atilhan[30] prepared hybrid DES with choline chloride as a HBA and urea, ethylene glycol, and glycerol as HBDs and explored their properties. This paper has prepared a DES shale inhibitor with high-temperature resistance, potent inhibition, and environmental protection, which can inhibit the hydration and dispersion of shale formation. First, this paper selected choline chloride quaternary ammonium salt as a HBA and urea and glycerol as HBDs to synthesize complex DESs named CGU-DES. In the preparation process of DES, choline chloride and different HBDs and their proportions will affect the physical and chemical properties of DES. When the molar ratio of choline chloride to urea and glycerol is 1:2, the obtained DES can generate a stable hydrogen bond network at a certain temperature (such as 70 °C, 80 °C, and 90 °C), so that its properties tend to be stable, which is conducive to industrial production and application. Therefore, the preparation of this paper refers to the above content.[31] The hydrogen bond formation of CGU-DES was characterized by Fourier infrared spectroscopy, and the target product CGU-DES was confirmed. Then, the high-temperature resistance of CGU-DES was analyzed by using a thermogravimetric experiment. Second, the inhibition ability of CGU-DES was evaluated using a Na-bent inhibition test and a shale rolling recovery test. Finally, based on microscopy analysis, zeta potential analysis, X-ray diffraction, surface tension analysis, etc., the mechanism of inhibiting shale hydration and dispersion is analyzed.

2. MATERIALS AND METHODS

2.1. Materials. Choline chloride(AR,98%), glycerol(AR,99%), urea(AR,99%), and Na2CO3(AR) were purchased from Aladdin. Shandong Weifang Boda Na-bent Co., LTD provided Na-bent. Emulsion polymer DS-301, antitemperature and antisalt polymer fluid loss additive RHPT-2, low-viscosity polyanionic cellulose, and polyamine inhibitor were purchased from Henan Longxiang Petroleum Additives Co., Ltd.

2.2. Synthesis of the DESs. Choline chloride is the HBA, and glycerol and urea are the HBDs. The two (choline chloride and glycerol; choline chloride and urea) were placed in a beaker with a molar ratio of 1:2 and stirred in a water bath at 80 °C at 300 rpm for 1 h until a uniform and transparent liquid was obtained.[32] The product was cooled down at 25 °C. The two synthesized products were named CG-DES (consisting of

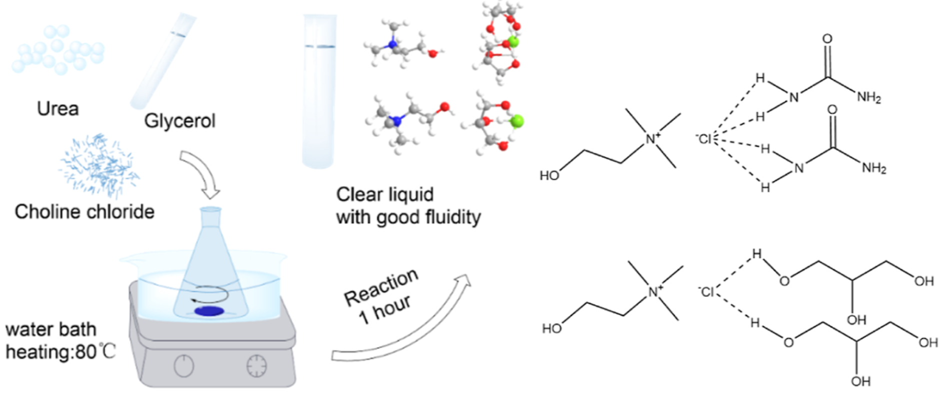

Figure 1. Schematic diagram of DES preparation.

choline chloride and glycerol) and CU-DES (consisting of choline chloride and urea). Choline chloride as the HBA, and glycerol and urea as the HBDs. The three were placed in a beaker with a molar ratio of 1:1:1 and stirred in a water bath at 80 °C at 300 rpm for 1 h until a uniform and transparent liquid was obtained. The product was cooled down to 25 °C. The synthesized products were CGU-DES (consisting of choline chloride, glycerol, and urea). The above content is shown in Figure 1.

2.3. Characterization. *2.3.1. FI-IR.* A Nicolet iS20 FT-IR spectrometer with a resolution of 2 cm^{-1} characterized the functional groups of DESs in the range from 4000 to 400 cm^{-1}.

2.3.2. Thermogravimetric Analysis. The thermal stability of the copolymer samples was measured using thermogravimetric analysis (TGA) on an analyzer (Q600 SDT, USA), which worked at the scanning rate of 10 °C/min under an atmosphere of air within the temperature range of 40 to 400 °C.

2.4. Inhibition Evaluation. *2.4.1. Shale Rolling Recovery Test.* 50 g of shale cuttings sieved by 6 to 10 mesh was put into aging tanks containing water and different concentrations of inhibitor solutions (DESs) and heated for 16 h in a roller heating furnace (Qingdao Haitongda) at 100 °C. The remaining cuttings were gathered with a 40 mesh sieve, gently rinsed with clean water, dried for 2 h in a 105 °C oven, and weighed. The rolling recovery rate is calculated as the mass of 40 mesh shale cuttings divided by the mass of the starting cuttings. The first rolling recovery rate was calculated using the following formula

$$R = \frac{m_2}{m_1} \times 100\% \tag{1}$$

where m is the recovery mass, g; R is the hot roll recovery, %.

Cuttings from the first rolling recovery experiment were put into aging tanks containing water and different concentrations of inhibitor solutions (DESs) and heated for 16 h in a roller heating furnace at 100 °C. The remaining steps are consistent with the above experiments to calculate the secondary shale rolling recovery rate.

2.4.2. Activity Test. The inhibitor's aqueous solution was configured and allowed to stand. A 7 mL sample was taken, placed the sample cup in the sample compartment, closed the lid of the instrument, sealed it, and waited for the vapor to reach equilibrium. The measurement button was pressed, waited for the buzzer to sound, and the data was read and recorded. The instrument used for the activity test was an HB-3D-type intelligent moisture activity meter.

2.4.3. Relative Inhibition Rate Test. Relative inhibition rate tests were carried out for each DES. In one test, 350 mL distilled water was first added into two stirring cups respectively. Then, 1.40 g EDS was added into one of the two cups. Finally, 0.84 g Na_2CO_3 and 21.00 g Na-bent were added into both cups. The mixture was stirred on a high-speed stirrer for 20 min, and kept closed at room temperature for 24 h. The φ_{300} was measured and read.

2.4.4. Surface Tension Test. There are many methods to measure surface tension, such as the capillary rise method, drop weight method, maximum bubble pressure method, hanging ring method, and so on. This paper adopts the hanging ring method: the ring will be immersed in the solution and then slowly pulled out of the solution; when it is about to leave the surface of the solution, the solution forms a thin film on the metal ring of the ring as the ring is pulled out of the liquid surface; the surface tension of the solution will prevent the ring from being pulled out, and when the liquid film ruptures, the tension of the ring will reach the maximum value. The automatic interfacial tensiometer (JYW-200A) will record this maximum value P.

2.4.5. Compatibility Tests. Different concentrations of CGU-DES were added to the base slurry and drilling fluid and then heated, and the changes before and after adding different concentrations of the reagent in the drilling fluid were compared, so as to explore the suitability of CGU-DES to the base slurry of water-based drilling fluid. The drilling fluid formula is as follows: 4%Na-bent + 0.25%Na_2CO_3 + 0.3% DS301 + 0.2%RHPT-2 + 2%SMC + 1%LV-PAC + 0.5% polyamine. The rheological parameters of the sample were measured using a ZNN-D6B electric six-speed viscometer (Qingdao Tongchun), which includes apparent viscosity (AV), plastic viscosity (PV), and yield point (YP). The following formulas determine AV, PV, and YP.

$$AV = \varphi_{600}/2 \quad (mPa{\cdot}s) \tag{2}$$

$$PV = \varphi_{600} - \varphi_{300} \quad (mPa{\cdot}s) \tag{3}$$

$$YP = (\varphi_{300} - PV)/2 \quad (Pa) \tag{4}$$

Where φ_{600} and φ_{300} are the readings of the rotational viscometer at φ_{600} and φ_{300} rpm, respectively.

2.5. Inhibition Mechanism Analyses. *2.5.1. Zeta Potential and Particle Size Distribution Test.* The zeta potential and particle size of a 4 wt % Na-bent suspension

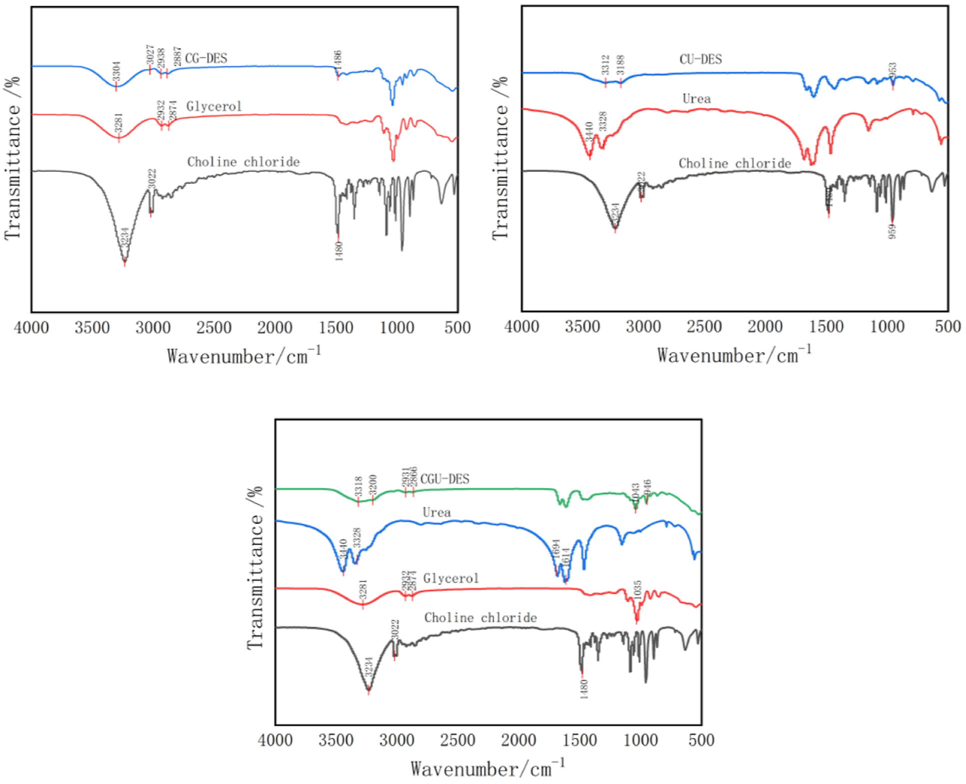

Figure 2. Infrared spectra of DESs.

containing different inhibitors were measured using a Zeta PALS 190 Plus, Brookhaven Instruments Corp., USA. Before the tests, the suspension needed to be ultrasonically dispersed for 5 min.

2.5.2. XRD. Different concentrations of inhibitors were added to 4 wt % Na-bent, stirred, settled for 24 h, and then centrifuged at 4000 rpm for 15 min; Na-bent precipitated at the bottom. An X-ray diffractometer analyzed the precipitations directly (Rigaku SmartLab SE, Japan).

3. RESULTS AND DISCUSSION

3.1. DES Characterization. *3.1.1. FT-IR Analysis.* Figure 2 displays the FT-IR spectra of several DESs. The chemical makeup of materials can be directly reflected by FI-IR, which can identify the presence of specific chemical bonds. Several new characteristic bands were generated in the spectra of several DESs compared with the initial HBA and HBD FT-IR. The DES spectrum overlaps with the other two spectra with slight differences. The formation of hydrogen bonds in DESs decreases the bonding constant K; the absorption peaks are shifted to lower wavelengths, and the peaks are broad, evidencing the formation of multimolecular intermolecular hydrogen bonding without the production of new compounds.

3.1.2. Thermogravimetric Analysis. Thermogravimetric analyses of prepared CG-DES, CU-DES, CO-DES, and CGU-DES were carried out. In Figure 3, the mass of CG-DES, CU-DES, and CGU-DES can still be maintained at about 95% of the original mass at temperatures lower than 175 °C, and according to the mass reduction, the temperature resistance is as follows from strongest to weakest: CGU-DES > CG-DES > CU-DES > CO-DES. The mass reduction rate of the samples was accelerated at temperatures higher than 175 °C, indicating that the DES structure was destroyed.

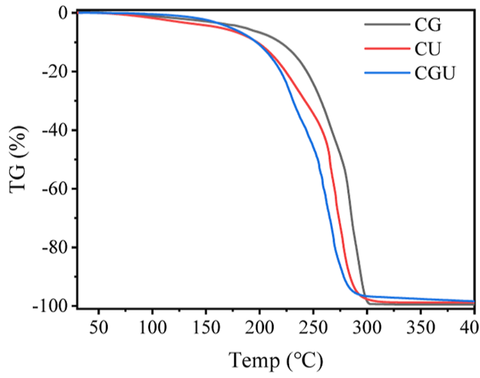

Figure 3. DES thermogravimetric analysis curve.

3.2. Inhibition Evaluation. *3.2.1. Shale Rolling Recovery Test.* The experiment is to simulate downhole conditions, mix shale samples with drilling fluid, and roll under a certain temperature and mechanical action to observe the dispersion and recovery of shale. The experimental results can reflect the inhibition ability of drilling fluids to shale hydration, dispersion, and settlement. In this paper, shale rolling recovery test experiments were used to investigate the effect of CGU-DES in inhibiting shale dispersion at 100 °C temperature. In Figure 4, from (a) to (c) is the effect of different concentrations of CG-DES, CU-DES, CO-DES, and CGU-DES aqueous solution on the rolling recovery of rock chips, (d) and (e) are the effect of DES aqueous solution on the shale rolling recovery of rock chips in the first shale rolling recovery rate and the secondary rolling recovery rate, respectively. The shale rolling recoveries increased dramatically when trace amounts of CGU-DES were added. The primary shale rolling recoveries were 98.04%, and the secondary shale rolling

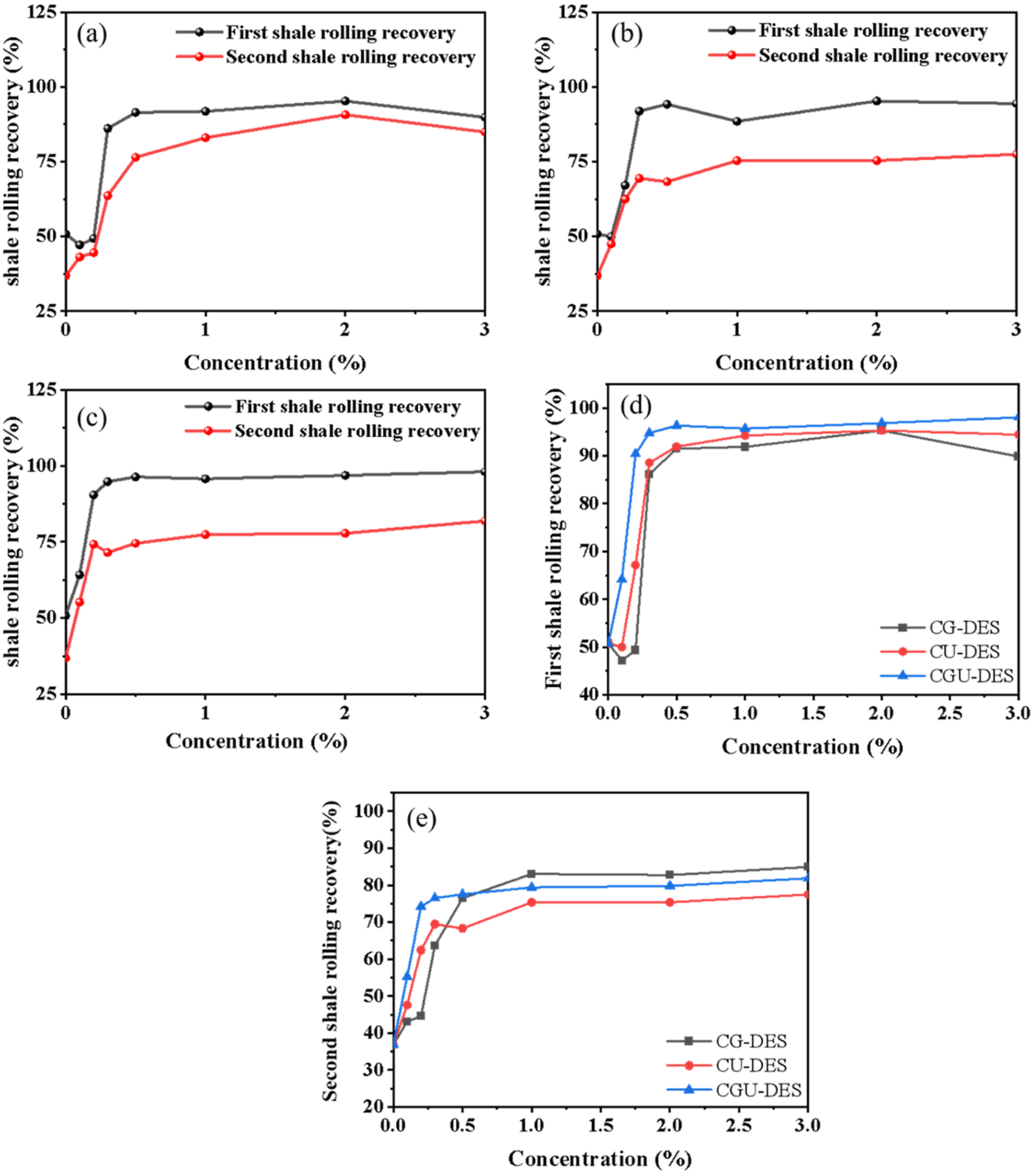

Figure 4. Shale rolling recovery of DESs.

recoveries were 78.08% when the dosage reached 3%, which were almost 1.5 and 2.4 times higher than those of fresh water. When the dosage was the same, CGU-DES had a relatively high primary shale rolling recovery compared with CG-DES, CU-DES, and CO-DES prepared from a single HBA and HBD.

3.2.2. Relative Inhibition Rate Test. In the hydration process of bentonite, the addition of inhibitors affects its rheology. This is because the addition of inhibitors may destroy or stabilize the network structure formed by bentonite particles, affect the yield stress and viscosity of the suspension, and then change the rheological properties. In this paper, a relative inhibition rate test experiment was used to investigate the ability of CGU-DES to inhibit the hydration and dispersion of clay minerals at room temperature. As shown in Figure 5, the relative inhibition rate can reach 100% when the dosage of CGU-DES is 0.5%, indicating that the low concentration of CGU-DES can effectively inhibit the hydration and dispersion of montmorillonite.

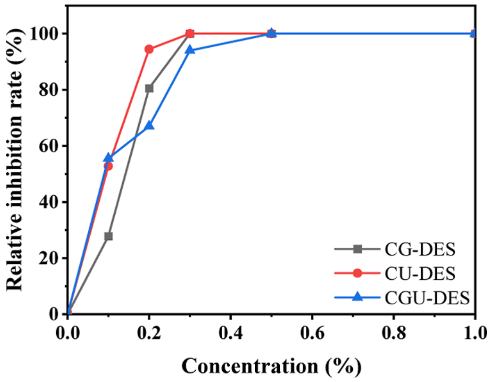

Figure 5. Relative inhibition rate.

3.2.3. Activity Test. According to the Donnan equilibrium theory and its derivatives, the very low permeability of mud shale can partially prevent the passage of solutes (ions) and act as a nonideal semipermeable membrane. The "chemical reverse osmosis" induced by the water activity difference helps to stabilize the excellent wall to a certain extent.[33] If the water activity in the drilling fluid is lower than the pore fluid activity of mud shale, chemical reverse osmosis can even cause the mud shale to lose water.[7] In Figure 6, CGU-DES can reduce the activity of aqueous solution very well.

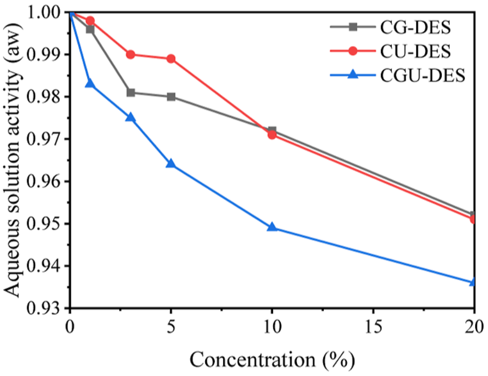

Figure 6. Aqueous solution activity of DESs.

3.2.4. Compatibility Tests. Different concentrations of CGU-DES were added into Na-bent slurry, polyamine drilling fluid, and polymer-sulfonated material drilling fluid after aggravation and hot rolling; with the increase of CGU-DES dosage, the thixotropy and AV of the aged drilling fluid became larger, and the dynamic-plasticity ratio tended to be more in the optimal range of 0.36−0.48 Pa/mPs, and at the same time, it could be observed that the reagent did not have any malignant effect on the water loss of API of drilling fluid. It can be concluded that the reagent DES is well adapted to polyamine drilling fluid systems and polymer-sulfonated material drilling fluids.

In Figure 7, compared to Na-bent. Slurry without CGU-DES, the AV, PV, ratio of yield point to plastic viscosity, filtration loss of the slurry after 120 °C and 150 °C aging increase with the increased amount of CGU-DES (0.5%, 0.7% and 1%).

In Figure 8, after adding 0.5%, 0.7%, and 1% of CGU-DES to the polymer-sulfonated material drilling fluid aging at 120 °C, 150 °C and 180 °C, the AV and PV of the polymer-sulfonated material drilling fluid slurry relative to the unadded CGU-DES increased with the addition amount. The kinetic-plastic ratio decreased to vibrate in the optimal range of kinetic-plastic ratios, and the amount of filtration loss did not change significantly. The filtration loss of the slurry after adding 0.7% and 1% CGU-DES aged at 180 °C was reduced from the original 34 mL to 28.4 mL, 23.6 mL, and 24 mL, in which the filtration loss reduction efficiency reached 30.59% when the CGU-DES dosage was 0.7%.

3.3. Inhibition Mechanism Analyses. *3.3.1. Zeta Potential Test.* The zeta potential of the dry Na-bent sample after hydration with deionized water was −20.8, and the zeta potential of the dry Na-bent sample after hydration with 3% aqueous CGU-DES solution became positive with a reading of 10.81, as shown in Figure 9. It can be seen that CGU-DES can effectively inhibit the dispersion of Na-bent.

3.3.2. Particle Size Distribution Measurement. The higher the degree of hydration of clay, the smaller the particle size. The effect of CGU-DES on the particle size distribution of Na-bent is shown in Figure 10. After the addition of CGU-DES, the particle size of Na-bent increased, and CGU-DES prevented the hydration dispersion of bentonite and promoted particle aggregation. CGU-DES weakened the stability of the system, compressed the electric double layer of clay, encouraged the aggregation of clay particles, and increased the particle size.

3.3.3. Scanning Electron Microscopy Analysis. Scanning electron microscopy was used to analyze the microscopic surface morphology of shale cuttings after unheated and hot rolling in clean water and CGU-DES solution (Figure 11). The surface of unheated rolling cuttings is irregular or angular (Figure 11a2), and pores are developed (Figure 11a1). After hot rolling in clean water, a large number of cracks can be seen on the surface of the shale cuttings (Figure 11b1). Enlarging the image further to 10,000 times, we can see that many small particles are broken (Figure 11b2), which is caused by the disintegration of shale after hydration and expansion. These fissures make it easier for water to invade the shale, which, in turn, can lead to shale disintegration and the collapse of well walls. In contrast, at the same magnification (Figure 11c1), shale rock chips rolled hot in CGU-DES solution have denser and smoother surfaces with no visible cracks. Figure 11c2 further explains why CGU-DES was able to inhibit fracture development in shale cuttings and achieve high recovery rates in shale rolling recovery experiments. CGU-DES forms a solid adsorbed polymer film on the surface of shale cuttings, blocking the micropores and cracks of shale cuttings, thereby preventing the intrusion of water and inhibiting the develop-

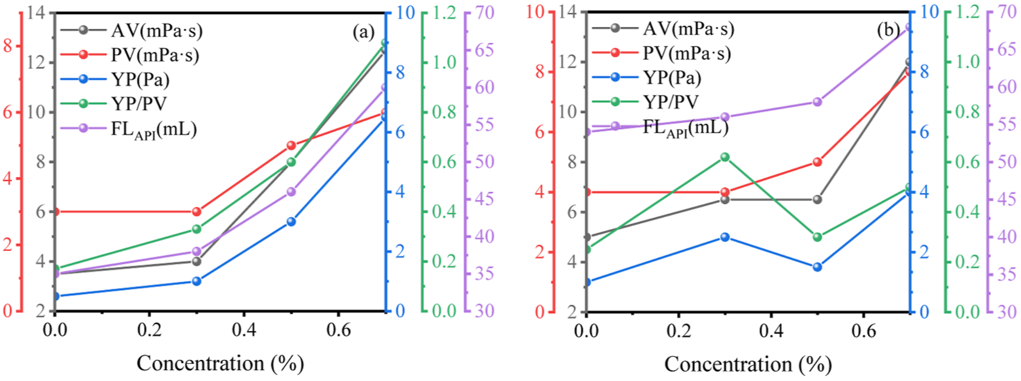

Figure 7. Effect of CGU-DES on the performance of drilling fluid base stock (a): hot rolling temperature is 120 °C; (b): hot rolling temperature is 150 °C.

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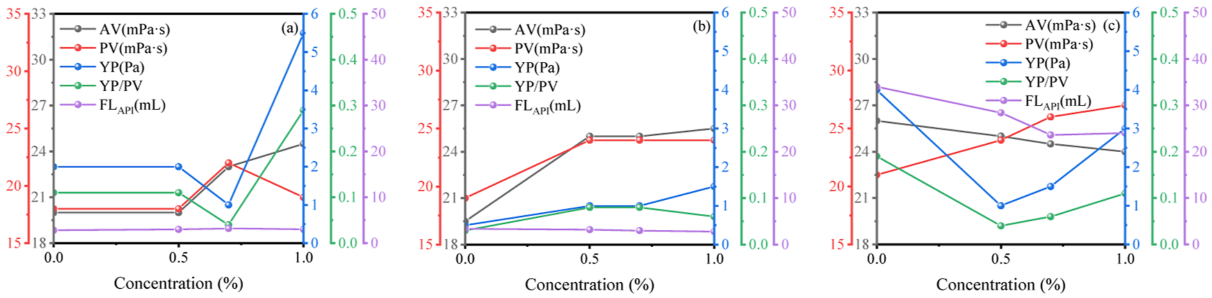


Figure 8. Effect of CGU-DES on the performance of drilling fluids with polymer-sulfonated materials (a): hot rolled at 120 °C; (b): hot rolled at 150 °C; and (c): hot rolled at 180 °C.

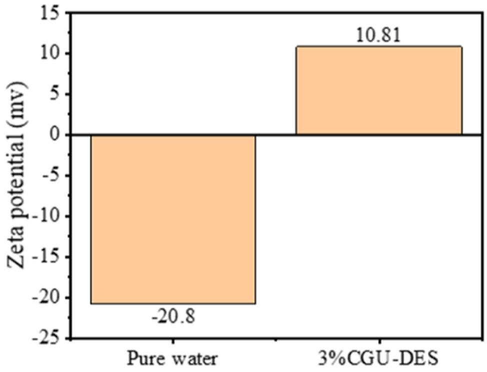
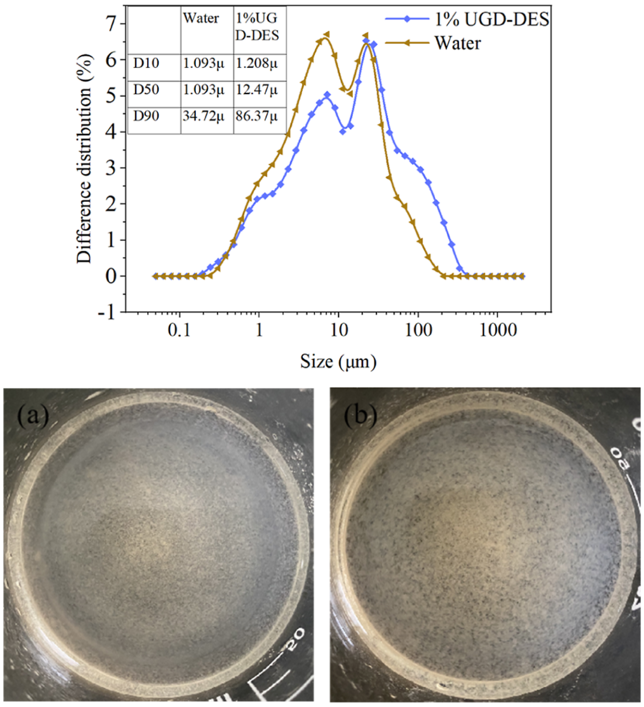


Figure 9. Zeta potential.



	Water	1%UGD-DES
D10	1.093μ	1.208μ
D50	1.093μ	12.47μ
D90	34.72μ	86.37μ

Figure 10. Effect of CGU-DES on the particle clay particle size distribution. (a) Pure water-dispersed sodium bentonite; (b) 1% CGU-DES aqueous solution-dispersed sodium bentonite.

ment of cuttings cracks. In this case, the shale cuttings can still maintain a large particle size in the CGU-DES solution, which is conducive to maintaining the stability of the shale wall and recovering the cuttings during drilling.

3.3.4. XRD. Figure 12 shows the $d_{(001)}$ of Na-bent with Na-bent modified with CGU-DES. The $d_{(001)}$ of the original Na-bent was 1.237 nm for the dry Na-bent sample. After the adsorption of CGU-DES, the d(001) of the Na-bent particles increased to 1.415 nm, indicating that CGU-DES was successfully inserted into the Na-bent interlayer.

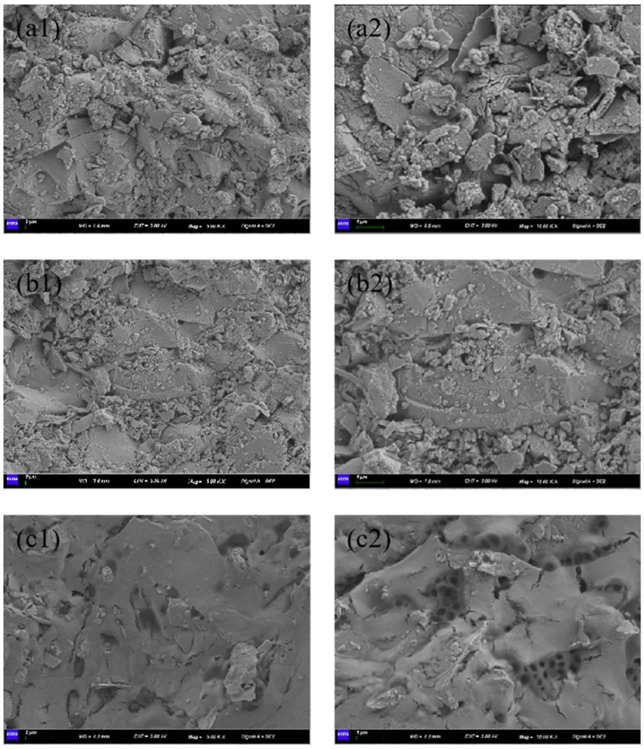


Figure 11. SEM image of shale cuttings (a) and its rolling recovery test in (b) clean water and (c) 5% CGU-DES solution.

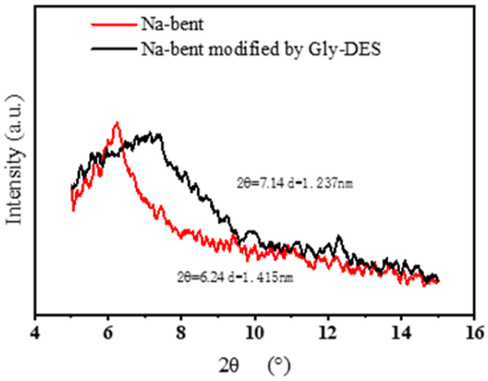


Figure 12. XRD patterns of Na-bent before and after CGU-DES modification.

3.3.5. Surface Tension Test.

The reduction in surface tension favors the reduction of the shale water uptake through capillary forces. In Figure 13, CGU-DES can effectively reduce the surface tension of the liquid, and the surface tension of CGU-DES aqueous solution was reduced by more than 30% when the dosage of CGU-DES was 5%, indicating that CGU-DES can effectively weaken the capillary force of shale, which helps to attenuate the capillary self-absorption effect of shale.[34]

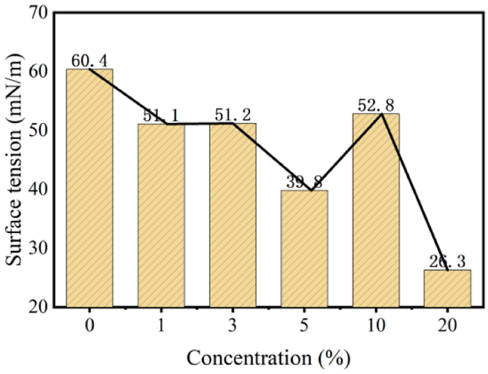


Figure 13. Surface tension of CGU-DES aqueous solution.

3.3.6. Contact Angle Test of Aqueous Solutions with Shales.

In Figure 14, the contact angle of the CGU-DES aqueous solution with the rock surface increases with increasing concentration. Therefore, the wettability of CGU-DES aqueous solution with the shale surface decreases relative to that of deionized water. This property of CGU-DES aqueous solution reduces the instantaneous water loss to a certain extent.

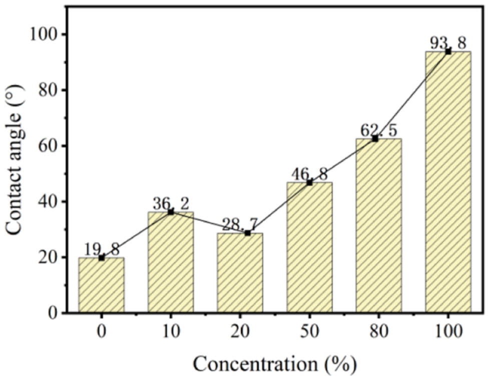


Figure 14. Contact angle between CGU-DES aqueous solution and shale surface.

3.4. Summary.

Shale formations are susceptible to well wall instability mainly because they are rich in clay minerals, and the main clay minerals susceptible to well wall instability are montmorillonite and illite. Montmorillonite has a layered crystal structure consisting of two Si−O tetrahedra and one Al−O octahedron, in which Al3+ undergoes lattice substitution with Mg^{2+}, resulting in a residual negative charge.[35,36] There are choline cations, hydroxyl, and amine groups in CGU-DES. The OH-groups in the glycerol as well as the chloride ion in the salt are capable of forming H-bonding between the constituents of the two DESs.[37] In Figure 15, the strong electrostatic attraction between the negative charge on the surface of montmorillonite and the choline cation causes the CGU-DES molecule to insert into the montmorillonite layer. The other end of CGU-DES has a hydroxyl group (−OH) and an amine group ($-NH_3$), which can form hydrogen bonds with the −OH or water molecules on montmorillonite to achieve interlayer free water. Thus, the expansion of the crystal layer caused by water molecules invading montmorillonite is reduced.[38,39] In Figure 16, the structure of CUG-DES makes it wrap on the surface of clay minerals through electrostatic attraction and hydrogen bond formation, and the hydrogen bond group at the other end forms a water film on the outside to realize the isolation of water molecules and clay minerals and achieve the purpose of inhibiting the hydration and dispersion of rock cuttings and well walls. CGU-DES can also weaken the shale capillary self-absorption effect by reducing the surface tension of the aqueous solution. CGU-DES reduces drilling fluid water activity. The "chemical reverse osmosis" induced by the water activity difference helps to stabilize the excellent wall to a certain extent. Therefore, DES can efficiently inhibit the hydration and dispersion of shale rock chips.

4. CONCLUSIONS

In this study, a novel hybrid low eutectic solvent, ChCl-Gly-Urea (CGU-DES), was designed and successfully synthesized

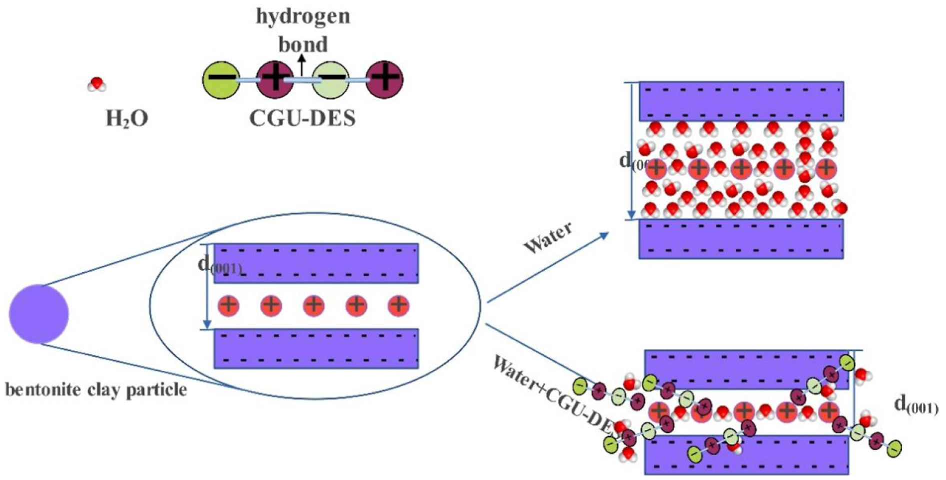


Figure 15. Mechanism diagram of CGU-DES inhibiting montmorillonite hydration.

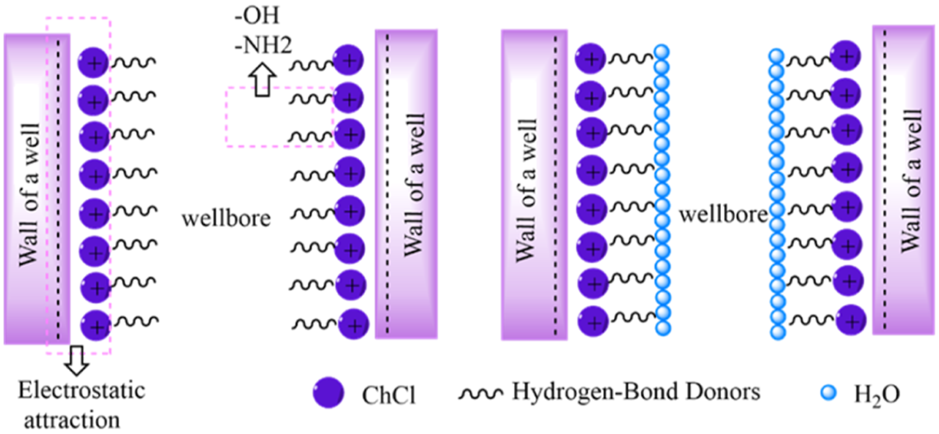


Figure 16. Schematic diagram of CGU-DES inhibition mechanism of wellbore instability.

and its application performance in water-based drilling fluids was comprehensively evaluated. First, this paper verifies that CGU-DES has the following advantages over CG-DES and CU-DES: better temperature resistance under 175 °C; in 3 wt % CGU-DES aqueous solution, the primary rolling recovery of shale was 98.04%, and the secondary rolling recovery of shale was 78.08%, which were 1.5 and 2.4 times higher than that of clear water and higher than that of CU-DES and CU-DES, respectively; the ability of CGU-DES to reduce aqueous activity was better than that of CG-DES and CU-DES, and CGU-DES can reduce the aqueous solution activity to less than 0.95 when the CGU-DES dosage is 10 wt %; CGU-DES can effectively inhibit the hydration and dispersion of Na-bent, and the relative inhibition rate can reach 100% when the dosage of CGU-DES is 0.5%; and CGU-DES has good compatibility with drilling fluid systems of sodic clay muds and polymeric sulfonated materials at 120 and 150 °C.

In addition, CGU-DES can efficiently inhibit the hydration and dispersion of shale rock chips, and the inhibition mechanism is as follows: (1) the choline cations in the CGU-DES quaternary ammonium salt molecules are adsorbed on the surface of negatively charged clay particles by electrostatic force, and the end of CGU-DES has a large number of hydrophilic groups, so it will bind free water by forming hydrogen bonds with water molecules to form a thin layer of water on the well wall, preventing free water from intruding into the wall and causing the shale wall instability; (2) hydrogen bonding and electrostatic attraction can cause DES molecules to insert into the interlayer of montmorillonite, thus reducing the swelling of the crystal layer caused by the intrusion of water molecules into the montmorillonite; (3) CGU-DES can reduce the capillary self-absorption effect of shale by lowering the surface tension of the aqueous solution; and (4) CGU-DES reduces drilling fluid water activity. The "chemical reverse osmosis" induced by the water activity difference helps to stabilize the excellent wall to a certain extent.

Potassium ions in KCl can replace intergranular cations in montmorillonite and inhibit the hydration of montmorillonite, but CGU-DES cannot. Therefore, this paper proposes whether CGU-DES can combine with KCl to form KCI-CGU-DES, which can inhibit the hydration dispersion and hydration expansion of shale through the combined action of replacing the intergranular cation of montmorillonite, surface adsorption, and binding free water.

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Notes

The authors declare no competing financial interest.

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