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# A Double Action P-D (Polymer-Deep Eutectic Solvent) Based Shale Inhibitor in Drilling Mud

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**ABSTRACT**

Shale stabilization is very significant during drilling to avoid wellbore stability issues. Water based drilling fluid results into shale swelling on contact with shale formation. Different additives are added in the drilling mud which inhibits the shale swelling by stabilizing the charge on the clay surface. Various polymers and different Deep Eutectic Solvents (DES) have been proven to be successful shale inhibitors, but their performance can be further improved by using a combination of polymer and DES. This research features a double action P-D (Polymer – Deep Eutectic Solvent|) inhibitor formulated by the combination of Potassium Carbonate based DES and modified oxazoline based polymer and compares its inhibition performance with KCl (Potassium Chloride). Linear Swell meter has been used after compressing the Na-Bt (Sodium bentonite) wafers at 1600 psia and swelling results have been analysed after 24 hours. Moreover, surface tension, d-spacing, and Zeta potential of inhibitors-based samples have been measured to justify and understand the swelling results. The results showed P-D inhibitor showed the best inhibition of 76% with maximum decline of 36% and 73% in Surface tension and Zeta Potential respectively. The double action of P-D inhibitor is associated with its capability to form hydrogen bond and exhibit Vander wall forces with the clay surface altogether.

## 1. Introduction

Shale formations are defined as low permeable and less porous sedimentary rocks consisting of different clays and mineral [1]. Their permeability and porosity depend on the type of clay, composition of clay and minerals present in it [2]. They also depend on textural characteristics of natural fractures, and anisotropy of bedding planes in the formation as well. Clay composition and minerals present are the most important parameters. Shale formation is organically characterized by the presence of kerogen (organic matter) and its thermal maturity. Its thermal maturity states the degree of transformation of organisms into organic matter [3].

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Clay minerals present in shale causes the shale formation to become reactive towards fresh water. When the formation is exposed to water, it swells during drilling operation. The swollen shale formation causes many wellbore instabilities [4]. Which produces increased non-productive time (NPT) and the drilling cost [14]. There are different types of clay minerals present in the shale formation i.e., montmorillonite and kaolinite. The montmorillonite is composed of illite, smectite and a mixed layer of illite/smectite. Kaolinite and illite tend to disperse in water and smectite have the tendency to swell in water. Smectite and illite/smectite mixed layer minerals have larger specific surface area and high imbibition abilities. So, the shale with high contents of these two minerals has strong hydration and will lead to shale swelling causing wellbore instability [5].

### *1.1 Shale Inhibition*

Shale inhibitors may stabilize clay either by chemical interaction or mechanical plugging. Mechanical interaction is usually carried out by nanoparticles or cellulose materials while chemical interactions is shown by inhibitors such as salts, polymers, ionic liquids etc. [6]. Chemical inhibition is usually related to to ion exchange, adsorption, intercalation into the interlayer space of clay. This chemical interaction neutralizes the negatively charged clay layer which is responsible for stabilized clay and hinders water invasion into clay layers thus halting shale swelling.

### *1.2 Recent Usage of Polymers as Shale Inhibitors*

Murtaza *et al.,* [7] have used quaternary ammonium gemini surfactant for clay swelling inhibition giving only 20% inhibition. Zhong *et al.,* [8] reported the use of Polyether Diamine & Formate Salts (Sodium-formate & Potassium-formate) with concentration of 3 wt% for shale inhibition in WBDF (water based drilling fluid). The inhibition efficiency measured was 74.5% at 77 °C because the polymer started degrading at 77 °C and desorbing from shale surface. Hanyi Zhong has used Amine Terminated Polyamidoamine (PAMAM) Dendrimers in WBDF for shale inhibition giving 70% inhibition results [9]. Ma *et al.,* [10] has used Polyampholyte DAM polymer as shale inhibitor in WBDF with 47% inhibition results.

### *1.3 Recent Usage of Des as Shale Inhibitors*

Jia *et al.,* [11] were one of the pioneers who utilized DES as shale inhibitors as a greener and cheaper alternative to traditional ionic liquids. Jia *et al.,* [11] used CM-DES: choline chloride and propanedioic acid with a molar ratio of 1:1 CP-DES: choline chloride and 3- phenylpropionic acid in a molar ratio of 2:1 and CIM-DES:Choline chloride, itaconic acid and 3- mercaptopropionic acid (molar ratio 2:1:1) which resulted into 68% , 58% and 58% shale inhibition. Ma *et al.,* [12] utilized Urea:ChCl, Oxalic Acid:ChCl, Citric Acid:ChCl and Glycerine:ChCl based DES which caused 65% , 63%, 61% and 78.5% swelling inhibition respectively. Rasool *et al.,* [13] utilized Potassium Carbonate:Glycerine based DES and achieved 87% shale inhibition using a free style experiment. Both DES and polymers are successful in inhibiting the shale swelling. Polymers mainly interact with the clay by electrostatic interaction while DES shows hydrogen bonding [14]. This research will use Potassium Carbonate and Glycerine based DES for its cost effectiveness and excellent ability to formulate hydrogen while for polymer, oxazoline based polymer will be used.

### *1.4 Modified Oxazoline based Polymer*

Oxazoline based polymer is a new class of polymers that is greener in nature, thermally stable and cost effective. Poly (2-ethyl-2-Oxazoline); POZ can perform the shale swelling inhibition more efficiently than the previously used polymers. The active site (–NH) will be making hydrogen bonds with the clay minerals to inhibit the hydration [15]. The structure of poly (2-ethyl-2-oxazoline) is given in Figure 1. In its modified form, the hydroxyl terminated poly (2-ethyl-2-oxazoline); POZ – OH, it has better hydrogen bonding capability as compared to POZ. In POZ – OH, the active site (–OH) is capable of making the hydrogen bonds [16]. The structure of this polymer is given in Figure 1.

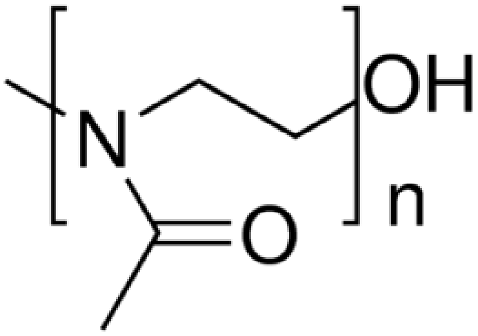


**Fig. 1.** Poly (2-ethyl-2-Oxazoline) hydroxyl terminated

Additionally, its degradation temperature is high i.e., 150 °C as compared to polyethyleneimine. It has been considered as an alternative of Polyethylene Glycol (PEG) with no accumulation properties [17]. Because PEG has accumulation traits that contaminate the other additives of drilling fluids e.g., nanoparticles. Due to this accumulation, they can't plug the pores of shale and these pores remain open to absorb water to always cause the shale hydration.

Polymers and DES have been used as shale inhibitors by various research groups and have proved their efficiency as potential shale inhibitors but polymers degrade at high temperature and DES alone doesn't give high inhibition results. In this research, a double action shale inhibitor (DES+Polymer) combined will be tested to evaluate its efficiency as a shale inhibitor. Both inhibitors are polars, so their combination is deemed to be soluble in mud. Moreover, the comparison of this double action inhibitor will also be carried out with the conventional inhibitor (KCl) and with DES and polymer alone. The characterizations such as Surface tension analysis, Zeta potential and basal spacing will also be found out to understand the underlying mechanism.

## 2. Methodology

The WBDF has been prepared by using 13B-1 API standards using the composition mentioned in Table 1. KCl is used as a conventional inhibitor and has been obtained from Sigma Aldrich, Malaysia. The monomers of modified PZ-OH have been purchased from Sigma Aldrich, Malaysia. Moreover, the in-house preparation of Potassium carbonate:Glycerine DES and selection of optimized concentrations can be studied in our previous work [14,18,19].

**Table 1**
Drilling fluid composition

| Component | Weight/conc./vol. |
|---|---|
| Bentonite | 22.5 g |
| Soda Ash | 0.25g |
| Caustic soda | 0.25g |
| Water | 350ml |
| Inhibitors | 0.5 % DES + 4% POZ-OH |

### *2.1 Sample Selection*

This research utilized refurbished pellet of bentonite approximately of 2.54 cm diameter which were made by compressing mass of 11.5 g of Na-bentonite powder at 1600 psi using a hydraulic press. The thickness of the pellets was measured. These pellets were then dipped in the drilling mud sample (base sample and sample with the inhibitors already incorporated) and the change in the thickness of pellet was determined by the Linear swell meter probe after almost 24 h.

### *2.2 Linear Swell Meter*

Grace HPHT Linear Swell Meter (M4600) had been used for the evaluation of shale swelling inhibition traits of prepared water-based drilling fluid. This apparatus has two separate components i.e., Wafer Compactor and Linear Swell Meter (Model: M4600). Wafers have been prepared using Grace core/wafer compactor while swelling tests have been conducted using the second equipment.

### *2.3 Surface Tension*

Surface tension is the tension present on the liquid surface due to cohesive forces. The invasion of the water in the shale is caused by the capillary action which is directly proportion to the surface tension [20] . IFT (Interfacial tensiometer) has been utilized to find the surface tension of the drilling fluid samples.

### *2.4 d-spacing (XRD)*

d-spacing is the sum of interlayer spacing between alumino silicate layers in clay and 1 one alumino-silicate layer. The wet drilling mud samples with 0.5% of KCl, DES and 4% of POZ-OH have been used to investigate the intercalation of all inhibitors into the clay layers by using X-ray diffraction (XRD) analysis. Benchtop X-ray diffractometer (D2 phaser) operating at 40 mA and 45 kV with Cu Kα radiation (λ=1.54059 Å) have been used to get XRD peaks for all wet samples. Bragg's equation was then used to find the d-spacing.

### *2.5 Zeta Potential*

Malvern Zetasizer Nano ZSP has been used to measure Z.P of the diluted drilling mud samples.

## 3. Results

### *3.1 Linear Swelling Test*

The percentage rise in swelling was noted for base mud, KCl, polymer, DES and P-D based mud. Figure 2 shows that base sample without any inhibitor resulted into a 63% increase in shale swelling. The swelling was reduced to 52% when KCl was included into the mud sample which further decreased to 31% and 19% for POZ-OH (Polymer) and (PC:Gly)DES respectively. The double action P-D inhibitor showed the best results with only 15% swelling as evident from Figure 2.

All incorporated inhibitors managed to inhibit the shale swelling up to some limit. KCl stabilized the shale swelling up to 17.4%, POZ-OH upto 51%, DES upto 70 % respectively. The double action P-D inhibitor showed best inhibition by inhibition the shale upto 76%. KCl majorly inhibits the shale swelling by the cationic exchange between clay layers. It expels the water's cations from inside the clay layers and makes the clay relatively stable. KCl based drilling showed the lowest swelling inhibition property, this is because KCl needs to be used in very high concentration to give optimum results, which outweighs its advantages. Polymers possess strong electrostatic force of attraction and can interact with clay with electrostatic force of attraction, thus neutralizing the clay which stabilized the shale hydration process. The double action P-D inhibitor contained both polymer and DES, its inhibition mechanism is mainly followed by both i.e., electrostatic interaction and hydrogen bonding with clay.

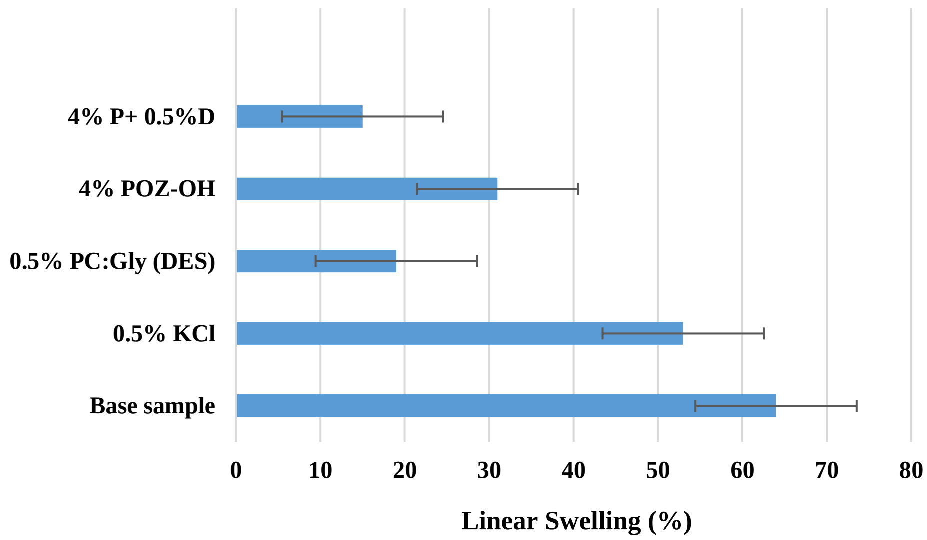


**Fig. 2.** Linear Swelling results after 24h

### *3.2 Surface Tension*

The anti-swelling properties of the clay can be well understood by analysing the surface tension of base mud and inhibitors based mud. Surface tension is directly proportion to the capillary pressure [21]. The greater the capillary pressure will be at the shale surface; the greater will be the tendency to water to invade into the clay layers and cause swelling [22]. The inhibitors can affect surface activity and reduce the surface tension, which hinders the water to invade into the clay layers. The maximum reduction in surface tension had been observed in case of double action P-D inhibitor while a 37% decline while 30% decline by DES and 9% decline by Polymer in surface tension has been observed. It is also worth noting that KCl based hydrated clay slurry showed the decline of only 3% as shown in Figure 3. The results are in accordance with the results of LSM.

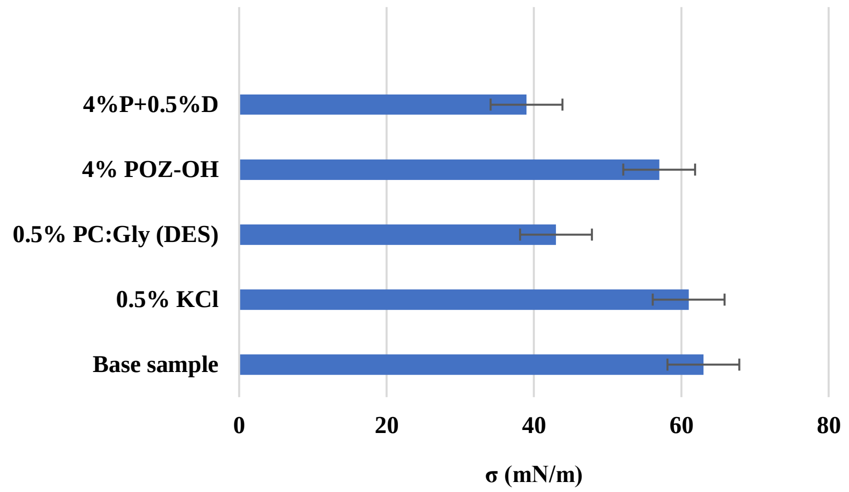


**Fig. 3.** Surface tension of inhibitors based samples

### *3.3 Zeta Potential*

Zeta Potential is a term that refers to electrokinetic potential in dispersion. The results of Zeta potential show the effect of inhibitors on thickness of electric double layer of the clay. Figure shows that the inhibitors reduced the electrical double layer which proves the cationic exchange between the inhibitors and the hydrated clay. The decline in ZP potential of KCl, DES, Polymer and P-D based samples was calculated to be 22.9%, 52.4%, 62.7% and 73% respectively as shown in Figure 4. The results of Zeta potential are further supported by d-spacing results in the next section.

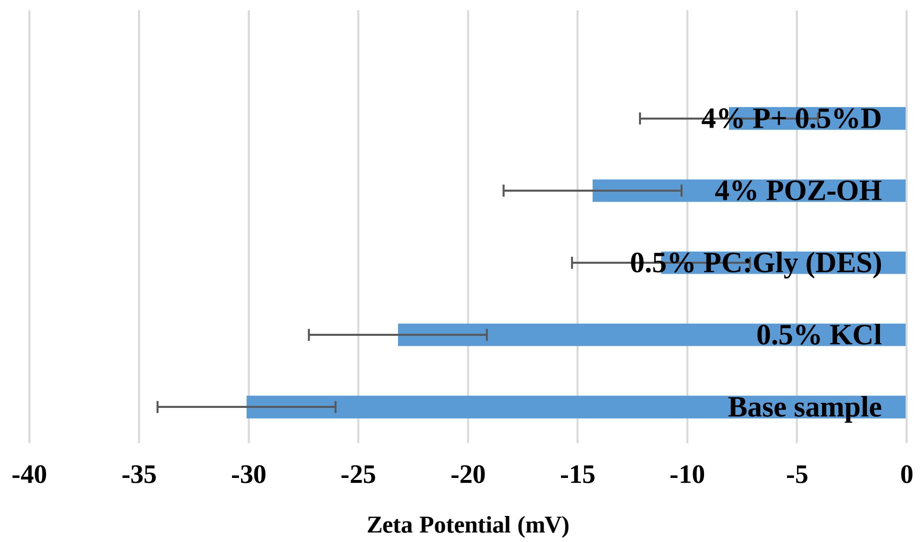


**Fig. 4.** Zeta Potential of mud samples

### *3.4 d-spacing (XRD)*

The d-spacing of the wet samples decreased by adding the inhibitor into the base samples, which confirmed the intercalation of inhibitors cations into clay layers. The d-spacing of dry Na-Bt came out to be 12.64 A° which rose to 18.01 A° after hydrating the dry Na-Bt. After adding the KCl, the cationic exchange between $K^+$, $Na^+$ and water cations started which decreased the d-spacing to 16.01 A° as shown in Figure 5.

The double action P-D inhibitor resulted into the maximum expulsion of water between the clay layers as shown by d-spacing of 13.01 A° while polymer and DES alone showed d-spacing of 14.5 A° 13.44 A° respectively. This decline in d-spacing values prove that the inhibitors have successfully intercalated between the clay layers and have expelled the water out from the clay layers. This also proves that added inhibitors possessed more affinity towards clay than water which makes them suitable for shale stabilization job and as per comparison the double action P-D inhibitor has shown the most affinity towards clay as compared to water and proved to be the best inhibitor in this study.

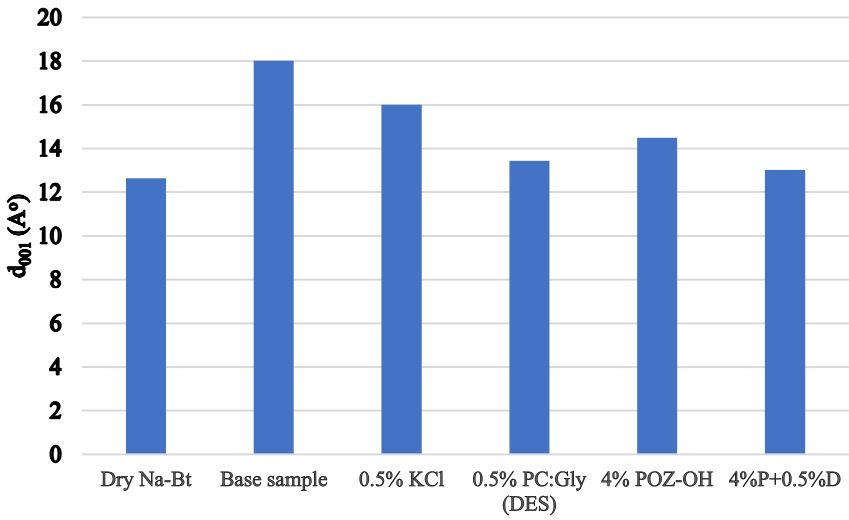


**Fig. 5.** d-spacing of mud samples

### *3.5 Discussion on Results*

Shale is an important source of unconventional fossil fuel but drilling shale causes a lot of problems [23]. In this study, HPHT Linear swell meter has been used to find the percentage swelling of clay to mimic the swelling activity in shale due to presence of montmorillonite clay. Since, KCl is a conventional inhibitor that has been currently used by industry, has inhibited clay swelling as per the experimentation but its inhibition tendency is less that as of the inhibition capabilities of polymer, DES and PD. This can be explained by the results of surface activity of hydrated bentonite in presence of KCl, DES and PD. DES and PD have resulted into an appreciable decline in surface tension which in turn depicts the decline in capillary rise and thus lesser invasion of water between clay layers. The results are further supported by the Zeta potential and d-spacing. The reduction in Zeta potential of inhibitors based sample shows the enhanced swelling inhibition ability of PD modified clay samples as reduction in zeta potential of clay is mostly correlated with its shrinkage and increase in Z.P refers to swelling. The results of d-spacing further support the conclusive results obtained from zeta potential. As the dry bentonite hydrates, d-spacing increases which shows the water has intercalated between clay layers but when inhibitors are added, they possess more tendency than water towards clay thus expelling water out from the clay layers. The PD based clay has showed maximum decline in S.T, Z.P and d-spacing thus proving to be an effective double action inhibitor.

## 4. Conclusions

Shale swelling results into wellbore instability during drilling and thus it must be controlled using suitable inhibitors as part of drilling mud. KCL, DES and PD as shale inhibitors have been used in this research and thus following conclusion have been drawn

i. Conventional inhibitor (KCl), DES, Polymer and double action inhibitor inhibited the shale swelling and among all inhibitors double action inhibitor (PD) gave the best inhibition result.
ii. A double action inhibitor interacts with clay with two different forces of attraction i.e., hydrogen bonding and Vander wall forces (electrostatic force of attraction) which justifies its effectiveness in shale stabilization.
iii. All inhibitors impacted the surface activity of the clay slurry and resulted into the decline in surface tension, which in turn decreased the invasion rate of water into the clay layers.
iv. The decrease in d-spacing values also demonstrate the effective intercalation of inhibitors between clay layers and PD inhibitor was able to expel the most water out from the alumino-silicate layers as compared to other inhibitors which were used in this research work.

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