Imidazolium-Based Ionic Liquids as Clay Swelling Inhibitors: Mechanism, Performance Evaluation, and Effect of Different Anions

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ABSTRACT: Clay swelling is one of the challenges faced by the oil industry. Water-based drilling fluids (WBDF) are commonly used in drilling operations. The selection of WBDF depends on its performance to improve rheology, hydration properties, and fluid loss control. However, WBDF may result in clay swelling in shale formations during drilling. In this work, the impact of imidazolium-based ionic liquids on the clay swelling was investigated. The studied ionic liquids have a common cation group, 1-allyl-3-methyllimidozium, but differ in anions (bromide, iodide, chloride, and dicyanamide). The inhibition behavior of ionic liquids was assessed by linear swell test, inhibition test, capillary suction test, rheology, filtration, contact angle measurement, scanning electron microscopy, and X-ray diffraction (XRD). It was observed that the ionic liquids with different anions reduced the clay swelling. Ionic liquids having a dicyanamide anion showed slightly better swelling inhibition performance compared to other inhibitors. Scanning electron microscopy images showed the water tendency to damage the clay structure, displaying asymmetrical cavities and sharp edges. Nevertheless, the addition of an ionic liquid to sodium bentonite (clay) exhibited fewer cavities and a smooth and dense surface. XRD results showed the increase in d-spacing, demonstrating the intercalation of ionic liquids in interlayers of clay. The results showed that the clay swelling does not strongly depend on the type of anion in imidazolium-based ILs. However, the type of anion in imidazolium-based ILs influences the rheological properties. The performance of ionic liquids was compared with that of the commonly used clay inhibitor (sodium silicate) in the oil and gas industry. ILs showed improved performance compared to sodium silicate. The studied ionic liquids can be an attractive alternative for commercial clay inhibitors as their impact on the other properties of the drilling fluids was less compared to commercial inhibitors.

1. INTRODUCTION

Clays are the most abundant and naturally occurring minerals. Clay minerals are composed of a phyllosilicate structure comprising of two layers of aluminosilicates. Each layer contained fused sheets of octahedral Al$^{3+}$, Mg$^{2+}$, or Fe$^{3+}$ oxides or sheets of tetrahedral Si$^{4+}$ oxides bonded together and synchronized by six oxygen atoms. The clay mineral in which one sheet of both tetrahedra and octahedra is arranged is named as T-O clay or sometimes called 1:1 clay. Meanwhile, if the two sheets of tetrahedra are sandwiching one octahedral sheet, then it is named as T-O-T clay or sometimes called 2:1 clay. Most commonly, clays are classified as 1:1- or 2:1-type clay mineral. The 1:1-type clay includes kaolin and chlorite group and is considered to be less prone to swelling, whereas the smectite or mixed-layer illite group (2:1-type clays) is considered to be most prone to swelling. In the smectite family, montmorillonite is the primary member, which is swellable and has a high cation exchange capacity (CEC), which could lead to hydration of clay mineral based on the cation type and pH of the fluid, whereas the illite group has a low tendency to swell, and the chlorite and kaolinite family has insignificant hydration capacity. Different types of clays have different swelling characteristics, and it is correlated with CEC; increasing the CEC leads to high swelling capacity.

Different types of swellable clays are present in shale formations that could result in a delay in drilling operations and increased construction cost of the well. The interactions of swellable clays in formations with water molecules present in the water-based drilling fluids (WBDF) lead to severe swelling.
problems. To prevent clay swelling, different types of swelling inhibitors are used as an additive in WBDF formulations. The clay swelling problems can also be avoided using oil-based drilling fluids. However, the associated higher cost, unfavorable for well logging, and ill-disposed environmental bearings lead to prohibiting the use of oil-based drilling fluids.

Conventionally, clay swelling inhibitors are electrolytes such as potassium chloride, sodium chloride, and divalent brine electrolyte. However, the higher concentration of these electrolytes causes coagulation of clay particles, which affects the characteristics of drilling fluids and causes increased fluid loss, loss of thixotropy, and environmental concern. To overcome these issues, polymer-salt combinations were proposed and used by several researchers. Polymeric used in drilling fluids as clay swelling inhibitors include low-molecular-weight polymers or oligomers such as polypropylene oxides (PPO) and polyethylene glycol (PEG). Some uncharged water-soluble polymers were employed to avoid clay swelling; the polymers can modify the properties of the drilling fluid and make it favorable to better the lifting capacity with smaller concentration. However, adsorption of polymer on the clay surface poses a major concern. Some charged polymers such as cationic, anionic, or zwitterionic polymers have also been reported in the literature for clay swelling inhibitors.

Clay inhibition behavior of amine-based drilling fluids was also investigated by many researchers. Some examples of these are polyacrylamide (PA), hydroxyethyl cellulose (HEC), and quaternary substituted HEC and their derivatives. The clay swelling inhibition of amines was adversely embellished by high-pressure and high-temperature drilling applications. Therefore, high-molecular-weight polymers, polymer nanocomposites, and nanoparticles were suggested to enhance the shale inhibition effectiveness at high-pressure and high-temperature drilling operations. Silicates, also known as protective silicate muds, are commonly used in the oil industry and have proven successful in drilling reactive shales; however, they fail to control the rheology and as protective silicate muds, are commonly used in the oil.

In the past two decades, the applications of ionic liquids have been investigated and proved in various fields attributable to their properties. Ionic liquids are admirable chemical and physical properties; some of them are low vapor pressure, specific solvating ability, high ionic conductivity, high thermal stability. Some cation groups of ILs are imidazolium, pyridinium, phosphonium, and ammonium, and some common anions are hexafluorophosphate, tetrafluoroborate, nitrate, octyl sulfate, chloride, bromide, and iodide. Several researchers have reported the performance of ILs on clay hydration and rheological properties.

One of the earlier investigations on the use of ionic liquids as clay stabilizers was reported by Berry et al. They used three ILs to evaluate inhibitive performance. The results suggested that ILs can substitute KCl in drilling fluids. Nasser et al. studied three ionic liquids labeled as 1-hexyl-3-methylimidazolium chloride (IL-1), 1-butyl-3-methylimidazolium octyl-sulfate (IL-2), and 1-butyl-3-methylimidazolium bromide (IL-3) for the clay inhibition and rheological behavior. The results from the experiments of rheology, XRD measurements, and zeta potential established that ILs can be used as clay swelling inhibitors. Moreover, the XRD confirmed that the ILs intercalated into the clay layers by the cation exchange mechanism. Luo et al. showed 1-octyl-3-methylimidazolium tetrafluoroborate as an improved shale inhibitor compared to KCl and polyamines. Yang et al. examined the inhibition capabilities of the 1-vinyl-3-ethylimidazolium bromide (VeIBr) monomer and its homopolymer. The results described the better capacity of both the VeIBr monomer and polymer against hydration of clays than KCl and amine-based inhibitors. In another study by Yang’s group, the effect of alkyl chain length of vinylimidazolium-based ionic liquids was explored, and the performance on the inhibition properties was studied. The results concluded that the IL with the ethyl group (shortest chain) offered better performance. In a recent study, Jia et al. considered the use of Gemini surface-active ionic liquids. They studied two imidazolium-based ionic ILs, 1-hexyl-3-methylimidazolium bromide (BMH) and its corresponding Gemini type, 1,2-bis(3-hexylimidazolium-1-yl) ethane bromide (HMH). The outcomes proved that both BMH and HMH efficiently prevented the shale hydration and swelling. The mechanism of ionic liquids in WBDF involves spontaneous adsorption of ILs on the negatively charged clay surface via electrostatic attraction, which contracted the electrical double layer of clay and strengthened the dispersion of clay.

Although ILs have recently been reported as swelling inhibitors, there is not a single field pilot application of ILs as swelling inhibitors. Several fundamental aspects of ILs as swelling inhibitors still need to be investigated. For example, the interactions of various cations and anions with different types of clays have not been reported. Similarly, there are very limited studies on imidazolium-based ILs as clay swelling inhibitors in drilling fluid applications and they need further investigation. There is not a single study that has investigated the effect of anions of imidazolium-based ILs on clay swelling inhibition. In this study, the application of imidazolium-based ionic liquids with different anion groups for WBDF was studied. First, the discussion of the results is provided. Then, the materials used and the experimental program are presented. The swelling inhibition performance was assessed using linear swelling tests, immersion tests, and capillary suction timer (CST). The mechanism of the swelling inhibitor was studied using contact angle measurements, particle size distribution, XRD, and SEM. In addition, the rheology and filtration behavior of drilling fluids modified with imidazolium-based ionic liquids having different anion groups were studied, and the results were compared with those of the base fluid. Furthermore, the effectiveness of the studied ionic liquids in contrast with commercially used clay inhibitor sodium silicate (Na2SiO3) was investigated.

2. RESULTS AND DISCUSSION

2.1. Linear Swelling of Clays. Linear swelling tests were conducted on the Na-Mt sample. In this study, 13 g of Na-Mt pellets was exposed to different concentrations of IL solutions. The IL solution (150 mL) was poured in a cup of linear swell tester, and the swelling measurement was recorded for 48 h.
Figure 1. Effect of concentration on linear swelling of 1A3MI-Br.

Figure 2. Effect of concentration on linear swelling of 1A3MI-I.

Figure 3. Effect of concentration on linear swelling of 1A3MI-Cl.
The swelling performance was compared with deionized water and commercially used Na₂SiO₃ solution. Figures 1−4 demonstrate the clay swelling results as a function of concentrations for four different ILs. The concentrations of ILs used in this experiment were 0.1, 0.3, and 0.5%. The swelling of the clay sample treated with ILs was much lower compared to the swelling by DI water (Figures 1−4). For example, after 48 h, the swelling was 180% for the clay treated with deionized water. However, the swelling percentage was reduced to 100% when the clay was treated with a 0.5% 1A3MI-CN solution. The reduction in clay swelling by the addition of ILs is associated with the adsorption of cation on the clay surface through the cation exchange mechanism. The cations of ionic liquids expel the sodium ions from the surface of the clay and adsorb on its surface. The organic nature of cation changes the hydrophilicity toward hydrophobicity. In all ILs used, we observed an inverse relationship between swelling and concentration. The increase in the concentration of ILs decreases the swelling percentage. Figure 1 shows the effect of concentration of 1A3MI-Br on linear swelling. It was noticed that the linear swelling rate declines with an increase in concentration. The results showed that by adding 0.1% 1A3MI-Br in the DI water solution, the linear swelling reduced from 180 to 146%. The results exhibit that further increase in concentration to 0.3 and 0.5% reduces linear swelling to 117 and 103%, respectively. This explains that the increasing concentration leads to an increase in ionic strength of 1A3MI-Br, i.e., the increases in ion concentration in the solution, which results in an increase in hydrophobicity due to the rise in organic cations. A similar trend was observed for 1A3MI-I, 1A3MI-Cl, and 1A3MI-CN, as presented in Figures 2−4, respectively. However, the effect of concentration was very significant for 1A3MI-Br and 1A3MI-CN. In the case of 1A3MI-I and 1A3MI-Cl (Figures 2 and 3), at an earlier time (for example, 10 h), the effect of concentration was noticeable. However, at a later time, the solubility of the solution has reached the saturation stage, and no further exchange of cations happens, which shows the negligible effect of concentration of 1A3MI-I and 1A3MI-Cl.
Furthermore, a comparison of different ILs at 0.5% concentration was performed with deionized water and commercial inhibitor (0.5% Na2SiO3) solution (Figure 5). The results showed that all investigated ILs showed comparable performance with the commonly used inhibitor Na2SiO3. At an early time period (5 h) of the linear swell test, the difference between the investigated ILs showed analogous behavior. However, at a later stage (24 h) of the experiment, it was observed that 0.5% 1A3Ml-CN showed comparatively better swelling inhibition compared to the other three ILs (0.5% 1A3Ml-I, 0.5% 1A3Ml-Br, and 0.5% 1A3Ml-Cl) and 0.5% Na2SiO3. The results showed that the anion has a minute effect on the inhibition properties of clay. Earlier studies revealed that unfavorable transfer between water and ions can influence the mechanical and physiochemical properties of clay and can cause the clay to swell.51 To overcome this issue, salts were used to decrease the water activity, thereby increasing solubility. Therefore, ionic liquids, which are organic salts, showed improved performance as clay swelling inhibitors.  

2.2. Immersion Test. The immersion test (free swelling) was conducted to further strengthen the observations of linear swelling tests. The Na-Mt pellets normally exhibited higher swelling when immersed in DI water compared to the treated solution, indicating high swelling ability and strong hydration of Na-Mt.26,49,53 In this work, we conducted the free swelling test where the Na-Mt pellets were exposed to different ILs in an open glass plate. Under room conditions (25 °C and 1 atm), 75 mL of each ILs was transferred into the glass plate containing Na-Mt pellets. The immersion test was carried out on all IL solutions. The images were taken at 5 min, 1 h, and 6 h to observe the behavior of free swelling in four different ILs, as shown in Figure 6. After 1 h exposure, there was no deformation in the sample treated with ILs, and all of them showed similar behavior. After 6 h, all ILs showed similar free swelling patterns, and 1A3Ml-CN showed comparatively better performance compared to others. The clay treated with ILs showed almost no disintegration after 6 h. However, commonly used inhibitors such as KCl can disintegrate the clay even after a short exposure. In our previous work, we found that the clay treated with KCl starts disintegrating even after exposure of 5 min and completely disintegrated after 5 h.39 The rate of deformation for the clay treated with KCl was very high compared to that for the clay treated with ILs. This is very important for field applications as disintegration can destabilize the shale, which could result in several operational problems. This shows the superiority of ILs over the commercial inhibitor.  

2.3. Capillary Suction Timer. The capillary suction timer (CST) test was performed to describe the effect of ILs on clay swelling inhibition. The CST test was used to characterize the inhibition and dispersion of clay. The high CST value describes a highly dispersed system having an impermeable filter cake, resulting in less free water, whereas the low CST value explains the flocculated system having a permeable filter cake, ensuring high free water.56 In this experiment, the time for the filtrate to flow across the fixed spaced electrodes was measured. Figure 7 presents the obtained CST values for base fluid and ionic liquid-based drilling fluids. It was noticed that base fluid caused high capillary suction time, whereas adding ILs to base fluid reduced the CST time. The lowest CST time was obtained in the 1A3Ml-CN base drilling fluid, subsequently followed by 1A3Ml-Cl, 1A3Ml-Br, and 1A3Ml-I. To compare the results, we tested the performance with 0.1% commercially used Na2SiO3. The results showed better performance of ILs compared with that of Na2SiO3. The results showed little effect of anion type in imidazolium-based ILs. The CST values obtained for ILs have a similar response as shown in the linear swelling test, except for 1A3Ml-Cl, which showed higher swelling.  

2.4. Particle Size Distribution. The particle size distribution probability and cumulative density probability are shown in Figure 8. It can be observed from the distribution density probabilities that adding ILs into the Na-Mt solution increased the particle size of the Na-Mt solution. The outcomes of data revealed that the addition of ILs favors Na-Mt agglomeration, resulting in the enlargement of particle size. However, the increase in particle size among different anion types in ILs was insignificant.  

2.5. Wettability Measurement. The contact angle provides the wettability behavior of the clay samples. In this experiment, a thin glass surface was coated with Na-Mt containing different IL solutions to measure the contact angle. To compare the results, a DI water-based fluid without ILs hydrated with the Na-Mt sample was prepared. Figure 9 shows the contact angle of different samples of ILs at 0.1% concentration. The base fluid result of contact angle measurement showed hydrophilicity behavior, showing a contact angle of 40.6°. However, the addition of ILs in the Na-Mt solution reduces the hydrophilicity as the contact angles increase, which reduces water interaction with clay. It was observed that no differences in contact angle measurements were observed when the anion of the IL is a halogen. However, small differences were observed when the anion is dicyanamide (CN). When ILs were added to the Na-Mt solution, the cation adsorbed on the surface and weakened the hydration of clays, increasing the contact angle. When ILs interact with Na-Mt (swelling clay), its cation adsorbs on the negatively charged surface, which reduced the double layer of Na-Mt particles and intensified the clay dispersion, the main mechanism behind clay swelling in ILs.17,49,50 However, the results showed that the anion type in the same cationic ILs also changed the wettability of clay particles to some extent but it was negligible. Earlier studies had shown that different anion groups on a common cation-based ionic liquid have little effect on the polarity.34 This advocates that the interaction between ionic liquids having different anion types and the clay decreases with an increase in the polarity of fluids.34–36 The reduced hydrophilicity of Na-

Figure 6. Photographic illustration of free swelling of Na-Mt in IL solution.
Mt treated with 1A3Ml-CN might be the consequences of this behavior on the Na-Mt surface. The high contact angle was obtained in 1A3Ml-CN, which further strengthens the results of linear swelling and capillary suction timer results. The contact of 1A3Ml-CN indicates slightly better inhibition performance followed by 1A3Ml-Br, 1A3Ml-Cl, and 1A3Ml-I.

2.6. X-ray Diffraction. X-ray diffraction is a common technique to study the crystalline structure of minerals and metals. In this technique, X-rays are used to interact with the material, which produce scattering and undergo various interferences; thus, diffraction into many directions can occur. X-rays are employed to study the basal spacing between planes of the crystal structure since the wavelength is typically the same order of magnitude (1−100 Å). The XRD patterns of dry Na-Mt and Na-Mt/IL dispersion are presented in Figure 10. It was noticed that the addition of ionic liquids increased

Figure 7. CST values for different ILs.

Figure 8. Distribution and cumulative densities of particle size for different IL solutions.

Figure 9. Contact angles for different ILs at 0.1% concentration.
the basal (d) spacing of Na-Mt. For 0.1% 1A3MI-Br, the basal spacing was enlarged from 12.40 to 13.14 Å. Correspondingly, the Na-Mt hydration in 0.1% solutions of 1A3MI-Cl, 1A3MI-I, and 1A3MI-CN enlarged its basal spacing from 12.40 Å to 13.248, 13.096, and 13.121 Å, respectively. This increase in d-spacing demonstrates the intercalation of ionic liquids in interlayers of Na-Mt. It was suggested that weak hydrogen bonding between Na-Mt platelets and water resulted in expelling of water molecules compared to the electrostatic interactions between the clay surface and ILs. The results are

Figure 10. XRD patterns of dry Na-Mt and dry Na-MT/ILs.

| Base mud | 0.1% - A3MI-Cl | 0.1% - A3MI-CN | 0.1% - 1A-3MI-I | 0.1% - 1A-3MI-Br |
|----------|----------------|----------------|-----------------|-----------------|
| a1       | b1             | c1             | d1              | e1              |
| a2       | b2             | c2             | d2              | e2              |

Figure 11. SEM images at different magnifications: (a1−c1) at 10 μm and (a2−c2) at 50 μm.

Figure 12. Illustration of the proposed mechanism for clay swelling inhibition using ILs.
in agreement with the literature, showing that adding ionic liquids leads to an increase in basal spacing.\textsuperscript{48,49} Therefore, the strong intercalation between the ionic liquid and clay surface was responsible for better inhibition performance.\textsuperscript{57} However, slight differences in basal (d) spacing were observed in different anions of ILs.

2.7. Morphology. To study the morphology of clay samples treated with ILs, SEM analysis was conducted. In this experiment, only three different samples were selected, i.e., base fluid without ILs, 1A3MI-Cl-treated sample, and 1A3MI-CN-treated sample based on the previous results. Figure 11 displays microstructure images of the base fluid and IL-based sample at two different microscales (10 and 50 \( \mu \)m). The SEM images presented an impenetrable and agglomerated structure for IL-treated samples compared to Na-Mt hydrated in DI water (Figure 12a–e). It can be observed from the images that bentonite treated with ILs provides a well-ordered structure and smooth surface compared to the nontreated sample. Earlier studies disclosed the effect of polarity on interlayer swelling, change in orientations, and evolution of the microstructure of swelling clays at the molecular scale.\textsuperscript{55} Furthermore, the results suggested that the cation type in ILs has little effect on swelling inhibition.

2.8. Mechanism. When water is exposed to the Na-Mt surface, it can be adsorbed into the interlayer of the clay, causing crystalline swelling and osmotic swelling. In the swelling process, Na\(^+\) would be substituted by water molecules and result in the expansion of the clay layer. The results obtained from the linear swelling inhibition test, immersion test, CST, particle size distribution, and contact angle measurements on the Na-Mt inhibition disclosed the improved inhibition performance of ILs. The addition of ILs in the Na-Mt solution increases the contact angle and particle size, which shows smaller water interaction with clay and improved coalescence capacity, resulting in improved inhibition and dispersion properties. Moreover, SEM images showed a well-ordered structure and smooth surface compared to the base fluid, which further strengthens IL inhibition performance. Furthermore, XRD results showed that the addition of ionic liquids increased the basal (d) spacing of Na-Mt, demonstrating the intercalation of ionic liquids in interlayers of Na-Mt.

Clay swelling inhibition mechanism using ILs is presented in Figure 12. When ILs interact with Na-Mt (swelling clay), its cation adsorbs on the negatively charged surface, which reduced the double layer of Na-Mt particles and intensified the clay dispersion, the main mechanism behind clay swelling in ILs.\textsuperscript{17,49,50} Moreover, the results showed that the anion type in the same cationic ILs has a minute effect on the inhibition performance of clay. Earlier studies revealed that unfavorable transfer between water and ions can influence the mechanical and physicochemical properties of clay and can cause the clay to swell. To overcome this issue, salts were used to decrease the water activity, thereby increasing solubility. Therefore, ionic liquids, which are organic salts, showed improved performance as clay swelling inhibitors.\textsuperscript{48,52}

2.9. Performance of Ionic Liquids in Drilling Fluids. The success of drilling operations depends on the performance of the drilling fluid. The drilling fluid used should have the capacity to carry cuttings and improve the hole cleaning. In addition, the drilling fluid should maintain wellbore stability and circumvent fluid influx from the wellbore. Different chemicals were used to obtain the desired property of the drilling fluid. The results from the previous swelling test showed improved performance of ILs as clay swelling inhibitors. In this study, the performance of four different ILs as additives on drilling fluids was investigated. The 0.1\% (w/v) ILs were used to prepare WBDF to study rheology and filtration properties. The results helped us understand the effect of ILs on rheological and fluid loss properties.

2.9.1. Rheological Properties. Rheology was used to describe the characteristics of the drilling fluid system. The rheology of the drilling fluid was studied based on the relationship between shear stress and shear rate. The pumping properties of the WBDF system were described by shear stress. In this study, we incorporated the shear rate used in the drilling operations. Shear rates in a drill pipe commonly include the range from 511 to 1022 s\(^{-1}\) (Fann speeds of 300 to 600 rpm), although in the annulus, flows are typically one to two orders of magnitude lower, ranging from 5.1 to 170 s\(^{-1}\) (Fann speeds
of 3 to 100 rpm). The shear stress and shear rate relationship for the studied ionic liquid-based drilling fluid is shown in Figure 13. We observed a decrease in measured shear stress as a function of shear rate when the ILs were added in the drilling fluid. A higher decrease in shear stress was noticed in 1A3Ml-Cl, whereas a smaller change was shown in 1A3Ml-Br compared to the base fluid. To compare the results, Na2SiO3 rheology was evaluated, and it showed a significant decline in shear stress. The results showed that different types of anions in imidazolium-based ILs affect shear stress. Earlier studies revealed that the anions (chloride, nitrate, and sulfate) could gather around the edge of the clay particles via physical adsorption (nonspecific adsorption), resulting in charge neutrality along the edges, thus reducing edge-to-face interactions, which results in a decrease in shear strength and a dispersive structure.52

The sharp decline in the viscosity of drilling fluids with an increase in shear rate describes the shear thinning behavior. The shear thinning behavior affects the efficiency of low-shear devices (centrifuges) and reduces the separation capacity. The viscosity of drilling fluids as a function of shear rate is plotted in Figure 14. It was noticed that the change in the slope of 1A3Ml-Br is higher compared to other ILs. The smallest change in slope was observed for base fluid, followed by 1A3Ml-CN. The results further support the application of 1A3Ml-CN as a clay swelling inhibitor in drilling fluids.

The basic rheological parameters include PV, AV, and YP. These parameters are associated with the performance of drilling fluids. The two viscosities (PV and AV) are related to the dynamic behavior of the fluid, and YP signifies the resistance to the initial flow. The ratio of YP/PV is important to characterize the behavior of drilling fluids. The ratio of YP/PV, also known as cutting carrying capacity (CC), implies the suspension and removal capacity of cuttings. Usually, the CC value greater than 0.75 (CC ≥ 0.75) demonstrates a good carrying capacity behavior of the drilling fluid, subsequently

![Figure 14. Viscosity vs shear rate of IL-based drilling fluids.](image-url)

![Figure 15. PV, AP, YP, and CC of different ILs.](image-url)
exhibiting an improved cleaning performance. Nonetheless, a high YP/PV indicates partial flocculation of solids, which may lead to loss of filtrate properties, blockage of the drill string, and annular frictional pressure loss upsurge, consequently increasing the equivalent circulating density (ECD) of the drilling fluid in the wellbore. From the literature, it has been recognized that YP/PV values should fall between 0.75 and 1.00 lbf/100 ft²/cP to guarantee effective wellbore cleaning while preventing an unwarranted increase in ECD.58,59 Figure 15 presents the PV, AP, YP, and CC of the IL-based drilling fluid. All studied IL-based drilling fluids showed better cutting suspension ability and good wellbore cleaning except for Na₂SiO₃. It was observed that sodium silicate has an adverse effect on the rheology of drilling fluids, whereas ILs showed better rheological performance. These outcomes supplemented our previous results; 1A3Ml-CN and 1A3Ml-I showed better performance. It was observed that the rheological properties of ILs changed by changing the anion type in the imidazolium-based ionic liquids. It was observed that anion type affects shear stress. Different types of anions in imidazolium-based ionic liquids affect their salinity. The similar behavior of anion effect on rheological properties was observed earlier, and it was suggested that salinity affects the dispersion characteristics of drilling fluids.48,60

To further characterize the effect of ILs on rheological parameters, the gel strength was measured at 10 s and 10 min as per API practices. The gel strength of drilling fluid is explained as the ability to hold the cuttings in suspension when the drilling operations are stopped or halted. The strength of the gel is correlated with cutting carrying capacity under static settings; low gel strength implies futile capacity. In contrast, high gel strength indicates a high pump pressure requirement during circulation. Once the cuttings tend to rapidly drop out from the drilling fluid to the bottom hole, it may cause severe problems, for example, drag and torque, a stuck pipe, and low rate of penetration.61 The results of gel strength for different ILs are shown in Figure 16. The gel strength at 10 s exhibits a nominal change except for 1A3Ml-Br and Na₂SiO₃. However,
the gel strength obtained at 10 min showed better performance of ILs compared to base fluid and commercially used Na₂SiO₃. It was interesting to notice that 1A3MI-I showed a higher value of gel strength (10 min) followed by 1A3MI-Br and 1A3MI-CN. It was noticed that the gel strength is also affected by the changing anion type in imidazolium-based ILs.

2.9.2. Filtration Tests. The API filtration properties were measured for IL-based drilling fluids using a filter press. The filtration behavior is critical since it identifies the amount of the filtrate volume that vanished into the rock formation. The high amount of filtrate loss is correlated with wellbore damage and instability problems. Figure 17 shows the results of filtrate volume (mL) obtained as a function of time (min) for IL-based drilling fluids at the filtration test period of 30 min. It was noticed that 1A3MI-Br showed lower filtrate volume compared to base drilling fluid, whereas all other IL-based drilling fluids exhibit higher filtrate volume. The commercially used Na₂SiO₃ showed higher filtrate volume loss. The filtration test also revealed the effect of anion type in imidazolium-based ionic liquids on the filtration characteristics. Although the filtration volume was slightly higher than that of the base fluid, it is still much lower compared to that of the commercial inhibitor Na₂SiO₃. Filtration results showed the disadvantage of sodium silicate; it can form a very thick filter cake, leading to high filtrate loss. Therefore, it is not recommended to use silicates in the reservoir section since it may lead to serious formation damage. The use of ILs has another advantage, in which they cause less filtration loss compared to commercial inhibitors. This can reduce the requirement of fluid loss additives in drilling fluids.

3. SUMMARY AND CONCLUSIONS

In this study, we systematically examined the four different ionic liquids (1A3MI-Br, 1A3MI-I, 1A3MI-Cl, and 1A3MI-CN) having the same cation but different anions for their clay inhibition capacity. The experiments considered to study clay inhibition include linear swelling test, free swelling test, CST, particle size distribution, wettability, and SEM analysis. Moreover, the performance of studied ILs as drilling fluids was assessed by rheology and filtration tests. The subsequent outcomes can be established from this study:

- All investigated ILs showed lower clay swelling compared to deionized water. The ILs showed comparable linear swelling with commercial inhibitors. The clay swelling reduction using ILs depends on the concentration of ILs used; i.e., the increase in concentration reduces the clay swelling.
- Unlike some commercial inhibitors, the ILs did not disintegrate the shale. This is extremely important for shale stability.
- For Na-Mt clay, the anion type has no significant effect. However, 1A3MI-CN showed improved swelling inhibition performance compared to other ILs.
- The CST values showed that adding ILs compressed the CST time, and it was lower compared to that upon adding the commercial inhibitor. The minimum time was attained for 1A3MI-CN solution that exhibited enhanced swelling performance among other ILs.
- The wettability of the bentonite samples showed a reduction in hydrophilicity with the addition of ILs as the contact angle of IL-treated samples increased.
- It was also noticed that the basal (d) spacing of IL-treated Na-Mt was increased, exhibiting strong intercalation in Na-Mt interlayers.
- The clay swelling does not strongly depend on the type of anion in imidazolium-based ILs. However, the type of anion in imidazolium-based ILs influences the rheological properties.

4. MATERIALS AND EXPERIMENTAL PROGRAM

4.1. Materials. In this study, four ILs, namely, 1-allyl-3-methylimidazolium bromide (1A3MI-Br), 1-allyl-3-methylimidazolium iodide (1A3MI-I), 1-allyl-3-methylimidazolium chloride, (1A3MI-Cl), and 1-allyl-3-methylimidazolium dicyanamide (1A3MI-CN), were purchased from Sigma-Aldrich. The molecular weights of 1A3MI-Br, 1A3MI-I, 1A3MI-Cl, and 1A3MI-CN are 203.08, 250.08, 158.63, and 189.22, respectively. The structures of ILs used are shown in Table 1.

Table 1. Structure of ILs

| IL          | Structure |
|-------------|-----------|
| 1A3MI-Br    | ![Structure](image)     |
| 1A3MI-I     | ![Structure](image)     |
| 1A3MI-Cl    | ![Structure](image)     |
| 1A3MI-CN    | ![Structure](image)     |

To investigate the clay swelling behavior, sodium bentonite (Na-Mt) was used. Na-Mt was provided by Halliburton Baroid. The composition of Na-Mt was examined using the X-ray diffraction (XRD) technique. Montmorillonite is the principal component of Na-Mt and has high swelling features. The cation exchange capacity (CEC) and surface area of Na-Mt were obtained as 81 meq/100 g and 710 m²/g, respectively. The composition of bentonite is presented in Table 2.

The performance of ionic liquids was compared with that of sodium silicate (Na₂SiO₃). Na₂SiO₃ was employed as a commercial clay inhibitor provided by Sigma-Aldrich. The drilling fluid solutions were prepared in deionized (DI) water.

4.2. Linear Swelling Test. Linear swell tests were performed to measure inhibition efficacy. In this test, the height of the clay pellet was measured as a function of time. The procedure involved placing 13 g of fine powder sample of Na-Mt into a pressure compactor, and then the pressure was applied up to 6000 psi by a hand pump for 30 min. After that, the cylindrical disc sample was prepared, and the pellet sample was loaded in the cup holder, then poured in 150 mL of prepared solution of IL, and rotated at 100 rpm during the experiment in a dynamic linear swell tester by OFITE (model #150-80-1). The linear height for a specific period was measured for every 30 s using the linear swell meter. The performance of the shale inhibitor was judged based on the minimum swelling of the Na-Mt sample. The optimal concentration of ionic liquids was estimated using this experiment. The swelling tests were conducted at three concentrations (0.1, 0.3, and 0.5 wt %) of the ionic liquid solution.

The linear swelling or expansion rate (LSR) is estimated with the given equation

$$ LSR = \frac{h_1 - h_0}{h_0} \times 100\% $$

(1)
where $h_0$ represents the initial height of shale pellet, and $h$, signifies the final height after immersing in deionized (DI) water and IL solutions for a given time $t$.

4.3. Free Swelling Test or Immersion Test. The free swelling test or immersion test was performed with Na-Mt pellet immersed in the IL inhibitor solution. The procedure of the free swell test involved placing a freshly prepared fluid solution with Na-Mt samples up to 24 h to observe clay stability. Different inhibitor solutions or DI water has different capacities for free expansion. Typically, a clay sample immersed in DI water indicates a high degree of expansion and swelling capacity by displaying cracks, erosion, and macropores, although samples immersed in IL inhibitor solution should result in less expansion volume and swelling capacity by showing less erosion, cracks, and pores as a result of developing a protective layer by ILs on the clay sample.

4.4. Capillary Suction Test. The capillary suction timer (CST) device was established by the Water Pollution Research Laboratory, England, to measure the time for the filtrate to travel across the electrodes when filter paper is in contact with suspension. This test was used to examine the colloidal properties of clay suspensions. The experimental procedure involved a sample being tested that was positioned inside the cylinder containing filter paper of a certain thickness, under which two electrodes (both coupled with a timer) were clamped and the time for the filtrate to travel across the electrodes was measured. The performance of clay inhibition was arbitrated based on the CST; less CST demarcated the good solution to avoid the hydration of clay and therefore prevented clay swelling.

4.5. Particle Size Measurements. The HELOS/BR Quixel Particle Size Analyzer was used to estimate the particle size of IL-treated Na-Mt solutions. The equipment can measure the particle size of suspensions and emulsions, ranging from 0.1 to 875 μm. In this test, the R1 range was selected to measure in submicron (0.1–35 μm). This instrument measured particle sizes using a laser diffraction method. The principle of the laser diffraction method described the scattering of the laser beam on a group of particles, where the particle size was inversely proportional to the angle of light scattering (i.e., the lesser the size of the particle, the greater the angle of light scattering). Particle size distribution provided an indirect measurement of clay swelling behavior. The increase in particle size by the addition of ionic liquid-based solution indicated the amalgamation characteristic of the ionic liquid.

4.6. Contact Angle Measurements. The contact angle measurement provided the information on the wettability of the solid surface by a liquid. The contact angle depends on the interaction and repulsion, which were the intermolecular forces and properties of the solid and liquid phases. The interactions of the solid and liquid phases were described by cohesion and adhesion. The contact angle at the solid—liquid interface was obtained when the balance between cohesive forces of similar molecules, for example, liquid molecules (van der Waals forces and hydrogen bond), and adhesive forces of dissimilar molecules, for example, liquid and solid molecules (electrostatic and mechanical forces), was established. When the cohesive forces were smaller than the adhesive forces, a small contact angle was obtained and vice versa. Most commonly, Young’s equation is used to give a contact angle. The contact angle was recorded by a Drop Shape Analyzer (DSA 100 provided by Kruss). The experimental procedure included preparing a thin layer of bentonite-dispersed solution on the glass surface and measuring the contact angle. The bentonite-dispersed solution was prepared with ILs and reserved for 24 h stirring. Once the solution was prepared, it was spread over a thin glass plate and dried overnight under ambient conditions. Then, it was placed in the equipment, and a little drop of water was released on the dried thin-layer sample. The equipment can measure the contact angle and take photos of the droplet. Large contact angles indicated a hydrophobic surface and were an indicator of clay swelling inhibition, while a small contact angle indicated the opposite.

4.7. X-ray Diffraction. In this study, the XRD system employed was the Empyrean model from PANalytical. In clay swelling studies, it was mostly used to examine the interlayer of Na-Mt by determining its basal spacing. Bragg’s equation $(2\sin \theta = n\lambda, \lambda = 1.5406 \text{ nm}, n = 1)$ was employed to calculate the interlayer (basal) spacing. The mixture was prepared using 2 g of bentonite in 0.1% concentration of ILs. The hydration was achieved by keeping the mixture for 24 h under atmospheric conditions. Then, the mixture was centrifuged at 6000 rpm for 30 min. The centrifuged mixture was dehydrated at room temperature and converted into powder for XRD analysis.

4.8. Morphology. In this study, the morphology defined the structural characterization of ILs with the interaction of clay (Na-Mt) samples. The characterization of the bentonite sample was achieved using scanning electron microscopy (SEM). SEM investigation involves scanning the sample with a focused electron beam to establish magnified images of the sample. The SEM images were recorded by Helios NanoLab G3 UC (FEI Corporation) at an accelerating voltage of 20 kV. The procedure involves first preparing the drilling fluid by blending bentonite and IL solution at high mixing speed. Then, the blend was kept for 24 h to achieve bentonite hydration in the IL solution. The blended sample was dried at room temperature and then carbon-coated before SEM measurements. At different magnifications, several images were obtained for analysis. The images obtained through SEM indicate the performance of different ILs based on the pore structure of the hydrated clay. If the SEM images exhibited an agglomerated and dense structure in the presence of ILs compared to hydrated bentonite in the base fluid, then they were considered to be good clay swelling inhibitors compared to the water-based fluid.

4.9. Rheology Measurement. Rheology described the flow and deformation characteristics of a fluid when a force was applied. It played a critical role in the preparation of the drilling fluid. The rheology of fluids provided important parameters such as properties of fluids and operating conditions, which help design a drilling fluid that can minimize the risk of hole cleaning and maintain wellbore stability. The 7 wt % bentonite sample was prepared with DI water and ionic liquid and stirred at high rpm for 30 min. The rheology of the
prepared solution was tested using an atmospheric viscometer developed by GRACE (model #M3600). American Petroleum Institute Standard (API-13B) was used to get the data. In this work, the sample in the viscometer was rotated at different rpm to record the shear stress. The rheological properties of fluid such as yield point, apparent viscosity, and plastic viscosity using a Bingham plastic model are determined by following relations (API, 1997)

\[
P V = \theta_{600} - \theta_{100} \quad (2)
\]

\[
AV = \frac{\theta_{600}}{2} \quad (3)
\]

\[
YP = \theta_{100} - PV \quad (4)
\]

where PV and AV define the plastic and apparent viscosities of fluid in cp, respectively; YP describes the yield point in lb/100 ft²; and \( \theta_{600} \) and \( \theta_{100} \) signify the dial readings at 600 and 300 rpm, respectively. Moreover, gel strength measurement was carried out under static conditions for 10 s and 10 min.

4.10. Filtration Test. The filtration test calculated the amount of mud filtration invasion to the formation and the thickness of the filter cake that was stocked on the formation when filtration occurred. The FANN Series 300 API LPLT filter press was applied to study filtration. Drilling fluid solution (350 mL) was placed in LPLT Filter Press, used under the room temperature of 25 °C, and the pressure of 100 psi was applied. The filtrate volume was collected in a cylinder from the LPLT filter press for 30 min. The frequency of data recording is 1 min for the first 5 min and every 5 min for the later 25 min. The amount of filtrate recovered describes the drilling fluid filtration characteristics.

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Notes
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Nomenclature

IA3MI-Br 1-allyl-3-methylimidazolium bromide
IA3MI-Cl 1-allyl-3-methylimidazolium chloride
IA3MI-CN 1-allyl-3-methylimidazolium cyanide
IA3MI-I 1-allyl-3-methylimidazolium iodide
AV apparent viscosity
CC carrying capacity
CST capillary suction timer
DI deionized water
ECD equivalent circulating density
FS free Swelling
IL ionic liquid
LS linear Swelling
PV plastic viscosity
SEM scanning electron microscopy
YP yield point

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