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Article

Effect of Alkylation Chain Length on Inhibiting Performance of Soluble Ionic Liquids in Water-Based Drilling Fluids

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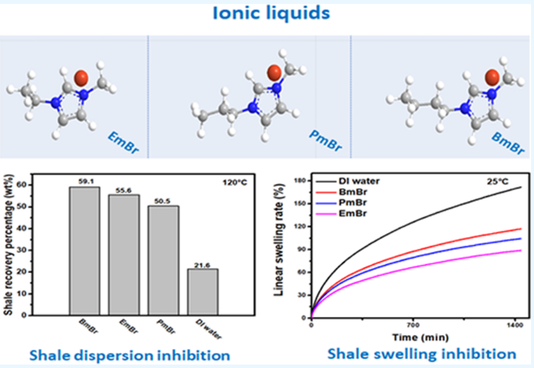
ABSTRACT: This work investigated the effect of the alkyl chain length of soluble methylimidazolium bromide ionic liquids (ILs) on their inhibition performance. The IL with a shorter alkyl chain length showed superior inhibition performance by suppressing clay swelling, mitigating clay dispersion, at room temperature. Particularly, the IL with an alkyl chain length of two (EmBr) reduced the sodium bentonite (Na-BT) swelling degree to 89% and achieved a cutting recovery of 81.9% after being rolled at room temperature, performing the best among all ILs. To systematically analyze the inhibition mechanism of ILs, X-ray diffraction (XRD), ζ potential, and particle size distribution have been carried out. The results revealed that the methylimidazolium with shorter alkyl chain length had better ability to enter the interlayer void by ion exchange and decrease interlayer distance, suppress the electrical double layer of the Na-BT particles and decrease the ζ potential, and promote the aggregation of Na-BT in water. It is also observed that high hot rolling temperature reduced the shale inhibiting performance of all ILs, and ILs with longer alkyl chain length had better ability to prevent cutting disintegration at high temperature. It is attributed to the variation of the hydrophilic characteristic of Na-BT at high temperature where EmBr no longer adsorbed the most on the surface and entered the interlayer voids of Na-BT. This study can be used as a reference to systematically explore the effect of the structure of shale inhibitors on their inhibiting performance and develop effective shale inhibitors.



1. INTRODUCTION

Shales now make up about 75% of the world's oil formations and are responsible for approximately 90% of wellbore instability problems.[1,2] They are rich in clay minerals, which are in the proportions of nearly 90%,[3] and are known for their hydrophilic character, resulting in swelling.

Clays are hydrous aluminum phyllosilicates, generally containing magnesium and iron. Montmorillonite (MMT), a typical swelling smectite clay mineral, is composed of succession of structural unit layers that is stacked by two tetrahedral silicate sheets encompassing an octahedral aluminate sheet. Isomorphous substitution in both sheets results in negative charges of MMT layers, which is compensated by exchangeable cations (e.g., Na^+ and Ca^{2+}) adsorbed on the surface of layers.[4] The cations, especially Na^+, readily hydrate in the presence of water, thereby forcing the clay layers apart by crystalline and osmosis hydration.[5] Typically, crystalline swelling can increase the interlayer space from 9 to 20 Å. Osmotic swelling can result in a further increase of 20 to 130 Å.[6,7] During the drilling process, the clay minerals in shale immediately adsorb water from water-based drilling fluids (WBDFs) and swell. The swelling of clays will in turn cause serious problems endangering the stability of the wellbore.[8−10] The most frequently encountered problems are (a) drilling fluid leakage in fragile areas that are poorly consolidated, (b) blocking of the drilling tool with a decrease in penetration rate, (c) contamination of the drilling fluid by clays, which disperse in the latter, leading to an increase in drilling fluid viscosity, (d) wellbore collapse, and (e) exorbitant drilling costs. The swelling of clays is therefore seen as a crucial problem that requires effective solutions. One of the solutions is the use of inhibitory drilling fluids such as oil-based drilling fluids (OBDFs).[11,12] However, the associated higher cost, unfavorable for well logging, and strong constraints due to environmental problems lead to prohibiting the use of OBDFs. Therefore, WBDFs containing effective inhibitive additives can replace OBDFs.

So far, the most common method to minimize the swelling of clays is the use of plugging and/or chemicals. Plugging

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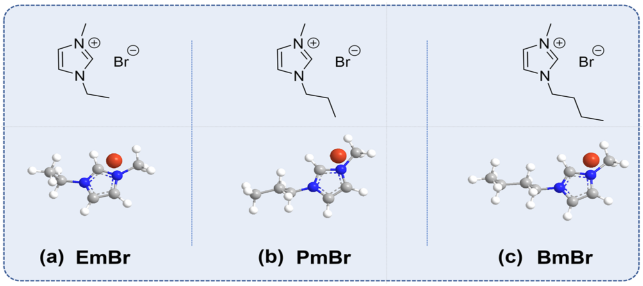
works by forming a thin film of solids near the wellbore can reduce water invasion into shale formation and minimize the exposure of clay minerals.[13,14] Compared with plugging, chemicals can interact with the shale surface, enter the interlayer region of the clay, and reduce the sensitivity of shale to water. In recent years, different chemicals have been used to inhibit the swelling of shale for drilling fluids, such as potassium chloride (KCl), amines, partially hydrolyzed polyacrylamide (PHPA), silicates, etc. Although these chemicals have shown effective inhibitive properties, they still have a few drawbacks, such as poor thermal stability, toxicity, ability to affect rheological and filtration properties of the mud, and environmental concerns. For example, KCl has been found to cause severe flocculation of clays used in WBDF and adversely affect the rheological and filtration properties of WBDF; moreover, the required high concentrations of KCl can affect the ecological system.[15,16] Amines[17,18] have been widely used in oilfields because of their excellent performances. Research studies have proven the effectiveness of PHPA[16,19] and silicates[20] in reducing and preventing the swelling of shale. Unfortunately, rheological problems and instability in high-temperature and high-pressure (HTHP) environments are often encountered when using PHPA and silicates. A new class of clay swelling inhibitors named "ionic liquids (ILs)" has been developed. The excellent inhibition properties of ionic liquids are comparable to those of polyamine and organic cationic polymers.

ILs are known as organic salts having ions poorly coordinated, which exist as liquids at low temperature (<120 °C). ILs have diverse chemical compositions and structures, and hence properties, which can be readily achieved by pairing a variety of cations with a wide range of anions. Common IL cations that have been studied include phosphonium, pyridinium, ammonium, and imidazolium. Comparably, the typically employed anion groups of ILs can range from hexafluorophosphate to tetrafluoroborate, octyl sulfate, nitrate, bromide, iodide, and chloride. ILs can be hydrophilic and hydrophobic depending on the structures of cations and anions.[21,22] In the past few decades, ILs have gained a lot of attention because of their remarkable physical and chemical properties, such as low vapor pressure, high thermal stability, specific solvating ability, compatibility with organic, inorganic, and polymeric materials, and so forth.[23−25] Due to their excellent properties, ILs have found many industrial applications, including chemical separation, metal extraction, dye adsorption, green solvents, nanocomposite preparation, etc.[23,26−28] Recently, ILs have been employed for many oil and gas applications, including enhanced oil recovery, CO_2 capture and sequestration, and extraction of heavy oil or bitumen.[29−31] In addition, numerous researchers[32−39] evaluated the inhibitive properties of ILs and demonstrated their great potential as effective shale inhibitors in WBDFs. In our previous work, the performance of the IL 1-vinyl-3-ethylimidazolium bromide (VeiBr) monomer and its corresponding homopolymers (PV) in inhibiting the swelling and dispersion of clays has been explored.[40] The result indicated the excellent inhibitory property of the VeiBr monomer and the superior inhibition effects of the PV polymer over the monomeric VeiBr. The PV polymer and VeiBr monomer exhibited better inhibition capacity than inorganic KCl and organic amine-based inhibitor (2,3-epoxypropyltrimethylammonium chloride). Recently, our group investigated the influence of anion type in vinylimidazolium-based ILs on the shale inhibiting performance. Several ILs with different anions such as bromide (Br^-), tetrafluoroborate (BF_4^-), hexafluorophosphate (PF_6^-), and bis(trifluoromethylsulfonyl) ($TFSI^-$) were systematically studied.[41] According to the results obtained, IL with a bromide anion exhibited remarkable shale inhibiting performance. In our other previous work, the influence of the alkyl chain length of the cationic part of vinylimidazolium-based ILs on the stabilization process of clays was studied.[7] IL with a short alkyl chain length displayed a strong inhibition performance by minimizing the swelling degree of clays and by preventing clays from disintegration. Similarly, many other researchers investigated the influence of the alkyl chain length on the inhibition performance of ILs. He et al. synthesized a series of imidazolium ILs with different alkyl chain lengths to inhibit the hydration and swelling of MMT.[34] It has been reported that at low concentration (<15 mmol/L), the longer the alkyl chain, the better the IL inhibition performance. Huang et al. studied the inhibitive properties of a series of synthesized imidazolium-based bola-form ionic liquids (IBFILs) with various alkyl chain lengths of even numbers (2, 4, 6, 8, and 10). The best inhibition performance on the hydration and swelling of shale was achieved from IBFIL with six carbon atoms.[35] However, solubility was one of the dominating factors to affect the inhibiting performance where ILs with too long alkyl chain length should be eliminated. It is important to conduct a study specialized in the inhibiting performance of soluble ILs irrespective of alkyl chain length of even or odd numbers.

In the present study, we explored the inhibiting properties of three soluble methylimidazolium bromide ILs with alkyl chain lengths of two, three, and four, attached to the imidazolium cation (Scheme 1). The three ILs were all soluble in water, which is the prerequisite for their shale inhibition performance. Furthermore, the molecular size of the three ILs might have an effect on their ability to inhibit the swelling of shale. The study on inhibition performance was carried out by linear swelling measurement, cutting recovery, and rheological properties. The inhibition mechanism of ILs was evaluated by XRD, ζ potential, and particle size measurement.

Scheme 1. Chemical Structures of (a) EmBr, (b) PmBr, and (c) BmBr



2. EXPERIMENTAL SECTION

2.1. Materials. 1-Ethyl-3-methylimidazolium bromide (EmBr), 1-propyl-3-methylimidazolium bromide (Pmbr), and 1-butyl-methylimidazolium bromide (BmBr) were purchased from Lanzhou Institute of Chemicals Physics, Chinese Academy of Sciences (China). Sodium bentonite (Na-BT) was supplied from Weifang Huawei New Materials Technology Co., Ltd. (China). The shale cuttings were obtained from

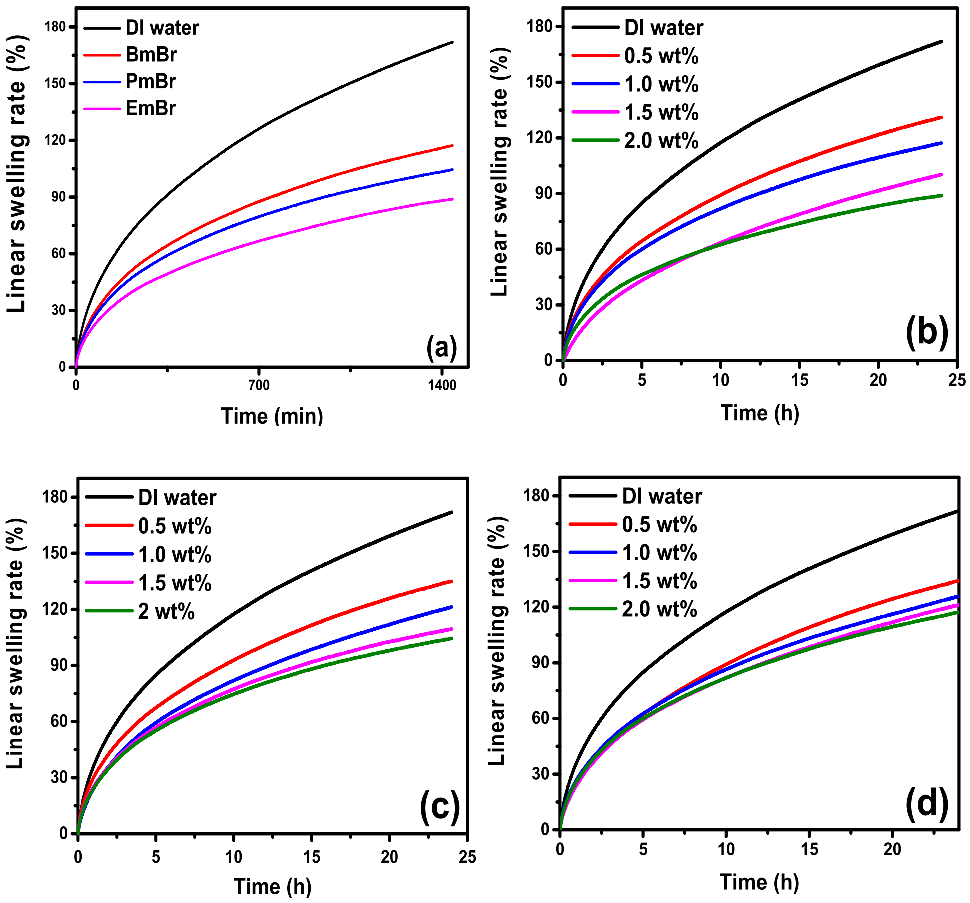


Figure 1. Linear swelling curves of the Na-BT pellet in (a) DI water and IL inhibitors at 2 wt % and (b) EmBr, (c) PmBr, and (d) BmBr at 0.5, 1.0, 1.5, and 2.0 wt % at 25 °C.

China National Petroleum Corporation Chuanqing Drilling Engineering Co., Ltd. (China).

2.2. Characterization of ILs. The chemical structures of ILs were confirmed by a ^{1}H nuclear magnetic resonance spectrometer (^{1}H NMR, AV 400 NMR, Bruker, US), referencing to deuterium oxide (D_2O) as the solvent with the signals recorded at $\delta = 4.79$ ppm, and a Fourier transform infrared spectrometer (FT-IR, Magna-IR 560, Nicolet, USA) in the wavenumber range from 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1}.

2.3. Inhibition Performance. Linear swelling test was used to assess the swelling behavior of the compacted Na-BT pellet after adding IL as a shale inhibitor. This test was performed at 25 °C. A total of 5 g of dried Na-BT was primarily compressed in a pellet for 5 min at 10 MPa using a cylindrical apparatus. Subsequently, the compacted pellet was placed on a linear swelling meter (CPZ-2, Tongchun China), and 20 mL of the IL solution at a concentration of 0.5, 1.0. 1.5, or 2.0 wt % was added to the Na-BT pellet. The pellet height was recorded every 30 s over time. The following equation was used to compute the swelling rate:

$$\text{linear swelling rate} = \frac{h_t - h_0}{h_0} \times 100\% \quad (1)$$

where h_0 is the initial height of the Na-BT pellet, and h_t is the final height after immersing in deionized (DI) water and IL aqueous solutions for a certain time t.

Recovery after the hot rolling test was used to evaluate the inhibition performance of ILs in preventing shale cuttings from dispersion. To carry out this test, 20 g of the initially sieved cuttings (approximately 2−3.1 mm in diameter) and 300 mL of IL inhibitor solutions at a concentration of 2.0 wt % were poured into a sealed jar. Then, the jar was hot-rolled in a roller furnace (BGRL-5, Tongchun, China) at 25, 40, 60, and 120 °C for 16 h. After cooling, the retained shale cuttings were screened with a 40-mesh sieve and washed with DI water to remove the shale fragments. Finally, the cuttings retained on the sieve were dried at 105 °C for 48 h. The recovery percentage of the shale cuttings after hot rolling was calculated according to the following equation:

$$\text{recovery percentage} = \frac{m}{m_0} \times 100\% \quad (2)$$

where m_0 is the initial mass weight of shale cuttings before hot rolling, and m is the final mass weight of the shale cuttings retained on the sieve after hot rolling and washing off.

To evaluate the inhibition effect of ILs on the hydrated dispersion of Na-BT, rheological measurements, including apparent viscosity (AV), plastic viscosity (PV), and yield point (YP), were calculated. Measurements were conducted using a ZNN-D6L rotary viscometer at 25 °C. Na-BT (12 g) was suspended into 300 mL of DI water or IL solutions. After stirring at 12,000 rpm for 30 min, AV, PV, and YP of Na-BT/IL solutions were obtained. For the upcoming measurements, the same quantity of Na-BT used before was added and stirred for 30 min until AV became unable to be recorded. The

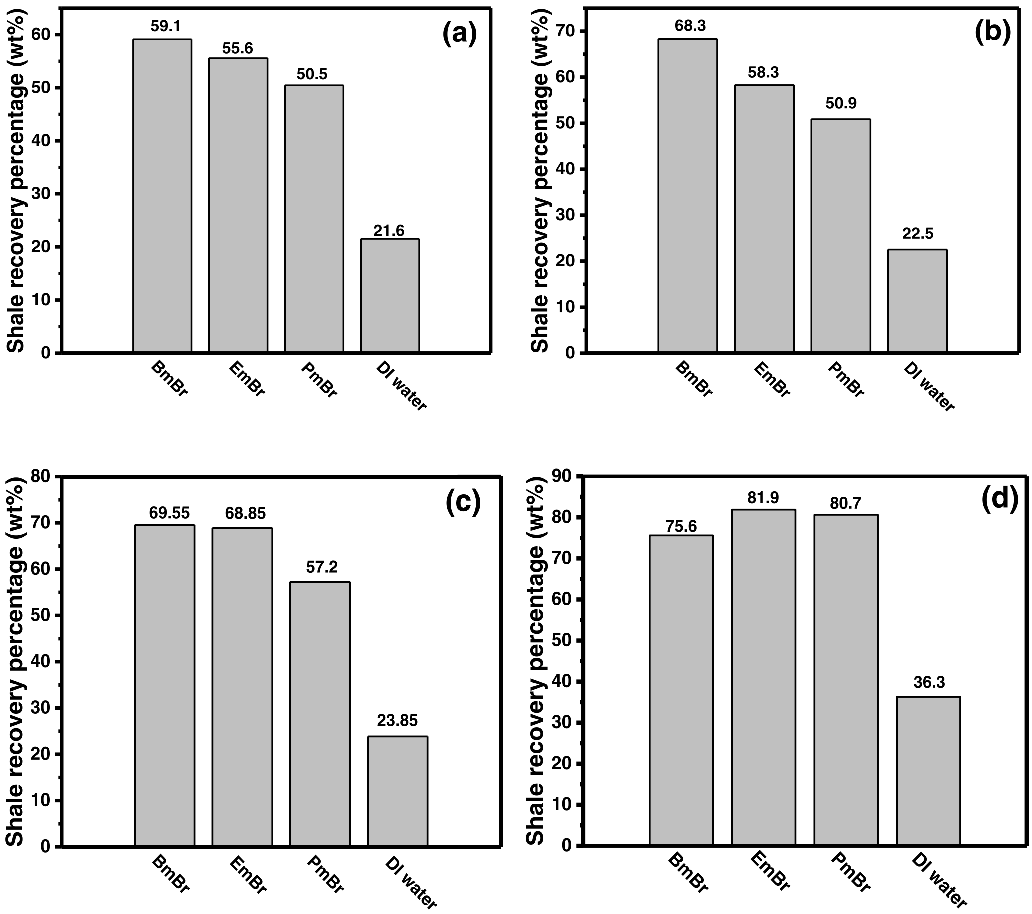


Figure 2. Recovery percentages of shale in inhibitor solutions at a concentration of 2.0 wt % after being hot-rolled at (a) 120, (b) 60, (c) 40, and (d) 25 °C for 16 h.

viscosity measurements were conducted at 600, 300, 200, 100, 6, and 3 rpm. The following equations were used to compute AV, PV, and YP:

$$AV = \theta_{600}/2 \tag{3}$$

$$PV = \theta_{600} - \theta_{300} \tag{4}$$

$$YP = 0.511(\theta_{300} - PV) \tag{5}$$

where $\theta_{600}$and θ_{300} are the viscosities at 600 and 300 rpm, respectively.

2.4. Inhibition Mechanism Analysis. On this aspect, XRD, ζ potential, and particle size distribution tests were carried out. IL solutions (4 mL, 2.0 wt %) were added into Na-BT suspension (4 mL, 4 wt %). The mixture obtained was used to carry out each of the aforementioned tests.

The IL/Na-BT mixture was stirred for 24 h, and the final precipitate obtained after centrifugation for 30 min was analyzed by X-ray diffraction (XRD, Rigaku, Japan). The generator voltage was 40 kV with the current of 20 mA. To calculate the interlayer spacing of Na-BT, the Bragg relationship was used.

$$d = \frac{n\lambda}{2\sin\theta} \tag{6}$$

where λ is the wavelength of the ray (Cu target: 1.5406 Å), θ is the angle between the screen and the ray, and n is a number.

The particle size of the dispersion of the IL/Na-BT mixture and Na-BT alone was measured at 25 °C using a Laser Scattering LA-960V2 (Horiba, Japan). The IL concentration in the prepared samples was approximately 10 g·L^{-1}.

The ζ potential was measured at 25 °C too using a Malvern Zetasizer Nano series (UK), and the IL concentration was approximately 1 g·L^{-1}.

3. RESULTS AND DISCUSSION

3.1. Inhibition Performance of ILs. *3.1.1. Linear Swelling Test.* One of the disadvantages of WBDFs is insufficient inhibitive property due to the existence of a large amount of water in the system. When a WBDF does not contain effective plugging materials and shale inhibitors, water tends to penetrate into the shale formations and induce the hydration and swelling of shale, resulting in wellbore instability. The linear swelling test is a method that consists of evaluating the inhibition performance of a given shale inhibitor compared to that of water alone. As shown in Figure 1, the swelling rate of the Na-BT pellet in DI water increased rapidly until it reached 172% after 24 h. However, after the addition of ILs, the swelling rate of the Na-BT pellet dropped considerably. It could be seen that EmBr exhibited the best inhibitive performance (Figure 1a). The swelling rates of the Na-BT pellet in 2.0 wt % EmBr, PmBr, and BmBr were 89, 104.5, and 117.25%, respectively. In addition, the swelling rate of the Na-BT pellet in IL aqueous solutions always decreased with the increase in concentration. For example, the swelling rates of the Na-BT pellet in 0.5, 1.0, 1.5, and 2.0 wt % EmBr were 131, 117.25, 100.25, and 89%, respectively.

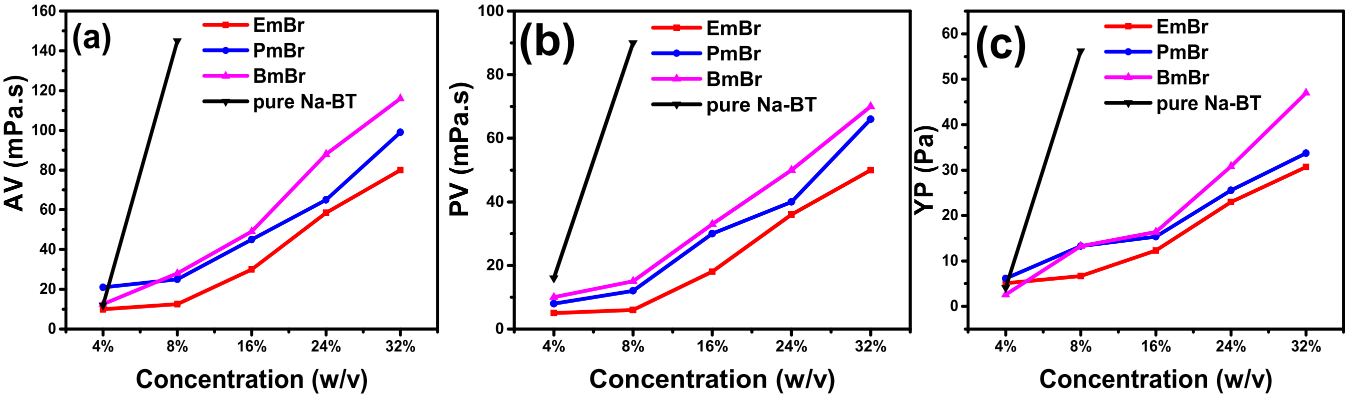


Figure 3. Na-BT inhibition test by comparing the AV (a), PV (b), and YP (c) of Na-BT dispersions added with ILs as a function of Na-BT content at 25 °C.

In this study, the alkyl chain length of ILs was in the following order: EmBr < PmBr < BmBr. IL with a longer alkyl chain length exhibited a poorer inhibition performance. It was primarily thought to be the result of the decrease in molar concentration as the alkyl chain length increases. Generally, when the chemical molecules perform similar inhibitory property, high molar concentration is favorable for inhibiting the performance. EmBr with the shortest alkyl chain length has the highest molar concentration when added at a same mass concentration and thus displays the greatest shale swelling inhibition performance. However, when EmBr was added at similar molar concentration to PmBr and BmBr, EmBr still showed better inhibitory property, probably due to its smaller molecule sizes and lower hydrophobicity, which ease the interaction with Na-BT and exchange of Na^+ in the interlayer voids of Na-BT. To certainly show the effectiveness of methylimidazolium ILs, the results were compared with those of vinylimidazolium ILs.[7] EmBr and PmBr had superior inhibition performance than all vinylimidazolium ILs, while BmBr presented similar inhibition performance. Therefore, the alkyl chain length has contributed to the improvement of the shale inhibition performance for methylimidazolium ILs.

3.1.2. Cutting Recovery after the Hot Rolling Test. This method was used to evaluate the inhibition performance of ILs in preventing shale cuttings against dispersion. The dispersion of shale cuttings in drilling fluids would seriously affect their rheological properties. The hot rolling test can simulate the movement of shale cuttings along the drilling fluids at high temperatures to evaluate the inhibitive properties of shale inhibitors. In our study, the shale recovery in DI water was only 21% after hot rolling at 120 °C for 16 h (Figure 2). When the shale cuttings were treated by IL inhibitors, distinct inhibition effects were achieved and the recovery was increased. The shale recovery values were 59.1, 55.6, and 50.5% in 2 wt % BmBr, EmBr, and PmBr aqueous solutions after being hot-rolled at 120 °C for 16 h, respectively. At high temperatures (40−120 °C), BmBr with the longest alkyl chain length provided the highest shale recovery value. Generally, a longer carbon chain in shale inhibitors could lead to better inhibitive efficiency as they could impede the water invasion by altering the clay surface to become more hydrophobic.[37,38] However, we could not provide an explicit explanation because we did not know the tendency of the inhibition mechanism due to the limitation of high-temperature measurements.

When the temperature decreased to 25 °C, the shale recovery was much higher in the presence of EmBr. The shale recovery values were 75.6, 80.7, and 81.9% in BmBr, PmBr, and EmBr, respectively. At room temperature, it was observed that the inhibition performance in shale recovery kept the same trend with the linear swelling rate. In this study, the inhibition performance and mechanism of ILs were all evaluated at room temperature (25 °C) except for the hot rolling test where high temperatures were used. The strong decrease in the interlayer spacing of Na-BT treated with EmBr (Figure 4) could explain the high performance of EmBr in shale recovery at 25 °C.

3.1.3. Rheological Measurements. Hydration and dispersion of clay minerals in drilling fluids might increase the bulk viscosity dramatically, and this may affect the penetration rate. Usually, clays have negative charge on the flat surface and positive charge on the edge. Clays could be linked together via three combinations, including the EE combination (edge-to-edge), the EF combination (edge-to-face), and the FF combination (face-to-face). The EF combination between the negatively charged flat surface and the positively charged edge of clays forms a "house-of-cards" structure, which is responsible for high viscosity. An effective shale inhibitor should be able to maintain a low rheological property of the mud. The experimental results of rheological properties are shown in Figure 3. It could be seen that when Na-BT was added at a concentration of 8 wt %, AV, PV, and YP were very high as a result of the increased EF combination and the friction between Na-BT and water molecules. However, when ILs (2.0 wt %) were added in advance, AV, PV, and YP were slowly increased with the increase in Na-BT concentration. Even at a concentration of 32 wt % Na-BT, the addition of ILs maintained the rheological parameters much lower than pure Na-BT dispersion at a concentration of 8 wt %. The influence of IL inhibitors on AV, PV, and YP could be explained by the fact that ILs can adsorb on the negative surface of Na-BT and prevent the disintegration; thus, PV were decreased. The disassembly of the previously formed structure resulted in a decrease in YP value. Therefore, AV was suppressed. Particularly, EmBr with the alkyl chain length of two showed the best inhibition performance on AV, PV, and YP of the Na-BT suspension, and increasing the alkyl chain length was disadvantageous. The inhibition performance of ILs on the viscosity provided a similar trend to the linear swelling rate and hot rolling (at 25 °C), in which EmBr exhibited the greatest inhibition ability among all ILs.

3.2. Inhibition Mechanism Analysis. *3.2.1. XRD.* XRD is a common technique to explore the crystalline structure of the material. When Na-BT is exposed to water, water will be directly adsorbed into the interlayer spacing (d-spacing) of the clay, leading to crystalline swelling and osmotic swelling. As mentioned early, crystalline swelling can increase the interlayer spacing from 9 to 20 Å, while osmotic swelling can result in a further increase from 20 to 130 Å. Thus, numerous clay swelling inhibitors work by decreasing the interlayer spacing and expelling water out of the interlayer of clays. Generally, a decrease in d-spacing indicates that water is expelled from the interlayer spacing; hence, inhibition performance is enhanced.[42] In our study, the d-spacing of Na-BT in distilled water was 14.71 Å, as depicted in Figure 4. When Na-BT is exposed to IL aqueous solution, the IL cations will enter the interlayer void by ion exchange with Na^+. It was noticed that the addition of ILs decreased the d-spacing to 14.33, 14.28, and 13.83 Å in BmBr, PmBr, and EmBr aqueous solutions, respectively. The decrease in d-spacing demonstrated the intercalation of ILs in the Na-BT interlayers, which resulted in the expulsion of water molecules due to the lower hydration ability of methylimidazolium compared to Na^+. The d-spacing was clearly affected by the alkyl chain length of ILs. EmBr with the shortest alkyl chain length performed a more effective decreasing effect on the d-spacing. Due to the higher hydrophilic property of EmBr, it had higher hydration ability in comparison to PmBr and BmBr. However, it was easier for EmBr to enter the interlayer void and decrease the interlayer distance because of the hydrophilic property as well as small molecular size. On the contrary, it was more difficult for PmBr and BmBr to enter the interlayer space, although PmBr and BmBr have lower hydration ability, which affected their inhibiting ability. In addition, the larger molecular size of PmBr and especially BmBr might have contributed to the increase in interlayer distance. The findings agreed with the previous studies, indicating that adding IL with a short alkyl chain length led to a decrease in d-spacing.[34,35] Although all the ILs studied in this work were water-soluble, the IL with the shortest alkyl chain length performed the best. Therefore, the strong intercalation between the shortest alky chain length IL and the clay surface was responsible for better inhibition performance.

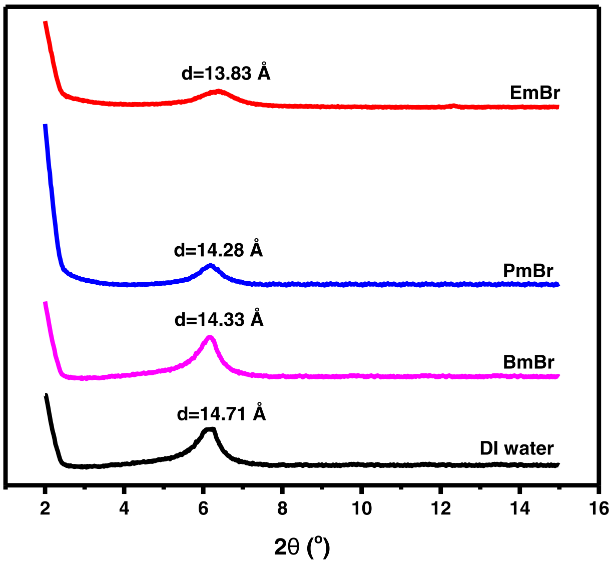


Figure 4. XRD patterns of Na-BT wet samples added with different IL inhibitors at a concentration of 2 wt %.

3.2.2. ζ Potential Measurement. The electrokinetic properties of Na-BT in the presence of ILs were investigated by measuring the ζ potential of the Na-BT particles in their aqueous dispersions, as shown in Figure 5. It is easier for clay particles with highly negatively charged ζ potential to swell and disperse. Na-BT took high net negative charges due to isomorphous substitution in the aluminum−oxygen octahedron. Generally, a ζ potential value greater than 30 mV indicates the sufficient stability of the particles.[43] In our study, the ζ potential value of Na-BT in DI water was −33.2 mV, showing considerable stability. After the addition of ILs, the ζ potential was reduced to −3.33, −5.80, and −8.86 mV in EmBr, PmBr, and BmBr aqueous solutions, respectively. It proved that the electrical double layer of the Na-BT particles was compressed and the stability of the Na-BT colloid was reduced. ILs can adsorb on the Na-BT particles and reduce the negative charge. Owing to the hydrophilic characteristic of the Na-BT surface, it is more attractive to hydrophilic ILs. A methylimidazolium cation can form hydrogen bonds with more than one Na-BT simultaneously, which further reduce the colloidal stability. As the alkyl chain length of IL decreased, the quantity of IL adsorbed onto the surface was increased; therefore, the ζ potential value was decreased closer to zero. The decrease in ζ potential reflected the less hydration, swelling, and dispersing ability of Na-BT, which is an important reason responsible for the shale inhibiting performance.

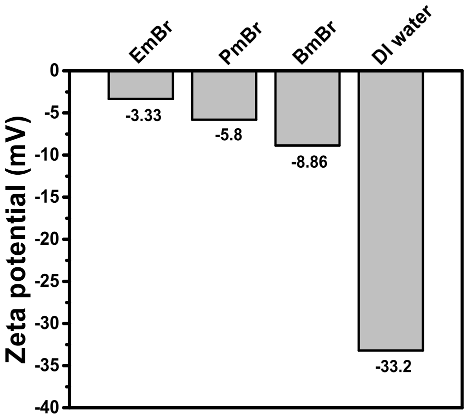


Figure 5. ζ potential measurement of Na-BT in DI water and IL aqueous solutions.

3.2.3. Particle Size Distribution. Clay will be dispersed into individual layers or small particles after being thoroughly hydrated in water, forming a stable dispersion system. The particle size of Na-BT in DI water in our study was 15.4 μm, exhibiting a bimodal distribution. An effective shale inhibitor can mitigate the dispersion of the clay and give rise to the aggregation of clay particles. As depicted in Figure 6, the addition of ILs markedly increased the particle size of the Na-BT dispersion to 36.7, 45.6, and 53.1 μm in BmBr, PmBr and EmBr, respectively. Accordingly, the inhibition of these ILs follows such an order: EmBr < PmBr < BmBr. This order was consistent with the ζ potential results. The largest size of the Na-BT particles in the presence of EmBr indicated the greatest ability of IL to prevent the dispersion of clays as the IL alkyl chain length decreased. In conclusion, the overall particle size results revealed that ILs can effectively agglomerate the

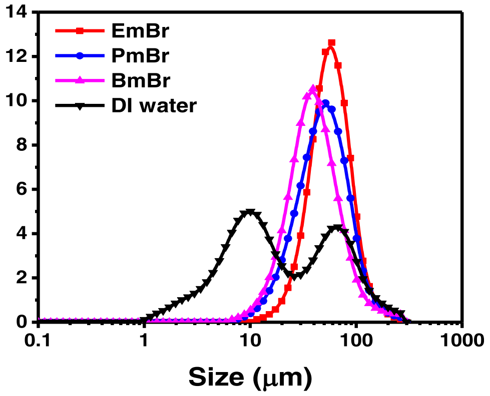


Figure 6. Particle size distribution of Na-BT in DI water and different IL aqueous solutions.

hydrated Na-BT particles, which were beneficial for the stability of Na-BT and shale.

4. CONCLUSIONS

This study examined the effect of the alkyl chain length of three soluble methylimidazolium bromide ILs with alkyl chain lengths of two (EmBr), three (PmBr), and four (BmBr) on their performance in inhibiting the swelling and dispersion of Na-BT. The excellent inhibition performance was achieved by decreasing the alkyl chain length of IL. The lowest linear swelling rate (89%) and the highest shale recovery (81.9%) at room temperature were displayed in the presence of EmBr, demonstrating the much better inhibitive properties of EmBr with the shortest alkyl chain length than those of PmBr and BmBr having the longer alkyl chain lengths. However, the shale recovery reached the highest values in the presence of BmBr at high temperatures, which is due to the higher hydration ability at higher temperatures, and too hydrophilic IL was not favorable to adsorb on the surface of shale cuttings. ILs have the ability to prevent the viscosifying effect when a large quantity of clay was dispersed in drilling fluids, which were frequently used in practical applications. The superior inhibiting ability of EmBr was attributed to the best ability to decrease the interlayer distance and lowest ζ potential and promoted the Na-BT aggregation, which was beneficial to shale inhibition. This work could be used as a reference to develop efficient IL-based shale inhibitors and other additives for WBDFs in the future.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c07796.

NMR and FTIR spectra of EmBr, PmBr, and BmBr (PDF)

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Notes

The authors declare the following competing financial interest(s): this is the revised manuscript.

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■ NOMENCLATURE

EmBr = 1-ethyl-3-methylimidazolium bromide
PmBr = 1-propyl-3-methylimidazolium bromide
BmBr = 1-butyl-methylimidazolium bromide
IL = ionic liquid
MMT = montmorillonite
Na-BT = sodium bentonite

■ REFERENCES

(1) Yue, Y.; Sa, C.; Wang, Z.; Yang, X.; Peng, Y.; Cai, J.; Nasr-El-Din, H. A. Improving wellbore stability of shale by adjusting its wettability. *J. Pet. Sci. Eng.* **2018**, *161*, 692−702.

(2) Guancheng, J.; Yourong, Q.; Yuxiu, A.; Xianbin, H.; Yanjun, R. Polyethyleneimine as shale inhibitor in drilling fluid. *Appl. Clay Sci.* **2016**, *127-128*, 70−77.

(3) Ahmed, H. M.; Kamal, M. S.; al-Harthi, M. Polymeric and low molecular weight shale inhibitors: A review. *Fuel* **2019**, *251*, 187−217.

(4) Chiu; Huang; Wang; Alamani; Lin. Intercalation strategies in clay/polymer hybrids. *Prog. Polym. Sci.* **2014**, *39*, 443−485.

(5) Johnston, C. T. Clay mineral-water interactions. *Dev. Clay Sci* **2018**, *9*, 89−124.

(6) Anderson, R. L.; Ratcliffe, I.; Greenwell, H. C.; Williams, P. A.; Cliffe, S.; Coveney, P. V. Clay swelling — a challenge in the oilfield. *Earth Sci.* **2010**, 201−216.

(7) Yang, L.; Yang, X.; Wang, T.; Jiang, G.; Luckham, P. F.; Li, X.; Shi, H.; Luo, J. Effect of alkyl chain length on shale hydration inhibitive performance of vinylimidazolium-based ionic liquids. *Ind. Eng. Chem* **2019**, 8565−8577.

(8) Ahmad, H. M.; Iqbal, T.; Al Harthi, M. A.; Kamal, M. S. Synergistic effect of polymer and nanoparticles on shale hydration and swelling performance of drilling fluids. *J. Pet. Sci. Eng.* **2021**, *205*, No. 108763.

(9) Muhammed, N. S.; Olayiwola, T.; Elkatatny, S. A review on clay chemistry, characterization and shale inhibitors for water-based drilling fluids. *J. Pet. Sci. Eng* **2021**, *206*, No. 109043.

(10) Sun, J. S.; Wang, Z. L.; Liu, J. P.; Lv, K. H.; Zhang, F.; Shao, Z. H.; Dong, X. D.; Dai, Z. W.; Zhang, X. F. Notoginsenoside as an environmentally friendly shale inhibitor in water-based drilling fluid. *Pet. Sci.* **2021**, 609.

(11) Razali, S. Z.; Yunus, R.; Rashid, S. A.; Lim, H. N.; Jan, B. M. Review of biodegradable synthetic-based drilling fluid: Progression, performance and future prospect. *Renewable Sustainable Energy Rev.* **2018**, *90*, 176−186.

(12) Zhou, D.; Zhang, Z.; Tang, J.; Wang, F.; Liao, L. Applied properties of oil-based drilling fluids with montmorillonites modified by cationic and anionic surfactants. *Appl. Clay Sci.* **2016**, *121*, 1−8.

(13) Huang, X.; Shen, H.; Sun, J.; Lv, K.; Liu, J.; Dong, X.; Luo, S. Nanoscale Laponite as a potential shale inhibitor in water-based drilling fluid for stabilization of wellbore stability and mechanism study. *Appl. Mater. Interfaces* **2018**, 33252−33259.

(14) Aramendiz; Imqam, A. Water-based drilling fluid formulation using silica and graphene nanoparticles for unconventional shale applications. *J. Pet. Sci. Eng* **2019**, *179*, 742−749.

(15) Li, X.; Jiang, G.; Shen, X.; Li, G. Poly-L-arginine as a high-performance and biodegradable shale inhibitor in water-based drilling fluids for stabilizing wellbore. *ACS Sustainable Chem. Eng.* **2020**, *8*, 1899−1907.

(16) Gholami, R.; Elochukwu; Fakhari, N.; Sarmadivaleh, M. A review on borehole instability in active shale formations: interactions, mechanisms and inhibitors. *Earth-Sci. Rev* **2018**, *177*, 2−13.

(17) Chu, Q. I.; Lin, L.; Zhao, Y. Hyperbranched polyethylenimine modified with silane coupling agent as shale inhibitor for water-based drilling fluids. *J. Pet. Sci. Eng* **2019**, No. 106333.

(18) Ma, J.; P, Y.; Yu, P.; An, Y. Research Progress on Shale Inhibitors at Home and Abroad in Recent Ten Years. *J. Oilfield Chem* **2019**, 181−187.

(19) Guecioucer, A.; Benmounah, A.; Sekkiou, H.; Kheribet, R.; Safi, B. Valorization of KCl/PHPA system of water-based drilling fluid in presence of reactive clay: application on Algerian field. *Appl. Clay Sci.* **2017**, 291−296.

(20) Mobeen Murtaza, M.; Kamal, M. S.; Mahmoud, M. Application of a Novel and Sustainable Silicate Solution as an Alternative to Sodium Silicate for Clay Swelling Inhibition. *ACS Omega* **2020**, 17405−17415.

(21) Houlton, S. Ionic Liquids: the Route to Cleaner and More Efficient fine Chemical Synthesis? *Chem. Week* **2004**, 3.

(22) Huddleston, J. G.; Visser, A. E.; Reichert, W. M.; Willauer, H. D.; Broker, G. A.; Rogers, R. D. Characterization and Comparison of Hydrophilic and Hydrophobic Room Temperature Ionic Liquids Incorporating the Imidazolium Cation. *Green Chem.* **2001**, 156−164.

(23) Dedzo, G. K.; Detellier, C. Clay minerals-ionic liquids, nanoarchitectures, and applications. *Adv. Funct. Mater.* **2018**, *28*, 2−3.

(24) Lei, Z.; Chen, B.; Koo, Y. M.; MacFarlane, D. R. Introduction: Ionic Liquids. *Chem. Rev.* **2017**, 6633−6635.

(25) Ren, Y.; Wang, H.; Ren, Z.; Zhang, Y.; Geng, Y.; Wu, L.; Pu, X. Adsorption of imidazolium-based ionic liquid on sodium bentonite and its effects on rheological and swelling behaviors. *Appl. Clay Sci.* **2019**, 2.

(26) Singh, M. P.; Singh, R. K.; Chandra, S. Ionic liquids confined in porous matrices: Physicochemical properties and applications. *Prog. Mater. Sci.* **2014**, 74−120.

(27) Srivastava, V. Ru-exchanged MMT Clay with Functionalized Ionic Liquid for Selective Hydrogenation of CO2 to Formic acid. *Catal. Lett.* **2014**, 2221−2226.

(28) Belbel, A. K.; Kharroubi, M.; Janot, J. M.; Abdessamad, M.; Haouzi, A.; Lefkaier, I. K.; Balme, S. Preparation and characterization of homoionic montmorillonite modified with ionic liquid: Application in dye adsorption. *Colloids Surf.* **2018**, 219−227.

(29) Pillai, P.; Kumar, A.; Mandal, A. Mechanistic studies of enhanced oil recovery by imidazolium-based ionic liquids as novel surfactants. *J. Ind. Eng. Chem.* **2018**, *63*, 262−274.

(30) Aghaie, M.; Rezaei, N.; Zendehboudi, S. A systematic review on CO2 capture with ionic liquids: Current status and future prospects. *Renewable Sustainable Energy Rev.* **2018**, *96*, 502−525.

(31) Berton, P.; Manouchehr, S.; Wong, K.; Ahmadi, Z.; Abdelfatah, E.; Rogers, R. D.; Bryant, S. L. Ionic Liquids-Based Bitumen Extraction: Enabling Recovery with Environmental Footprint Comparable to Conventional Oil. *ACS Sustainable Chem. Eng.* **2020**, *8*, 632−641.

(32) Ahmed Khan, R.; Kalam, S.; Norrman, K.; Kamal, M. S.; Mahmoud, M.; Abdulraheem, A. Ionic Liquids as Clay Swelling Inhibitors: Adsorption Study. *Energy Fuels* **2022**, 3596−3605.

(33) Ahmed Khan, R.; Murtaza, M.; Abdulraheem, A.; Kamal, M. S.; Mahmoud, M. Imidazolium-Based Ionic Liquids as Clay Swelling Inhibitors: Mechanism, Performance Evaluation, and Effect of Different Anions. *ACS Omega* **2020**, 26682−26696.

(34) He, Y.; Zhou, L.; Gou, S.; Jie, Y.; Gao, Q.; Siying, P.; Zhang, Q.; Wu, Y. Synergy of imidazolium ionic liquids and flexible anionic polymer for controlling facilely montmorillonite swelling in water. *Mol. Liquids* **2020**, 2−11.

(35) Huang, P.; Jia, H.; Han, Y.; Wang, Q.; Wei, X.; Luo, Q.; Dai, J.; Song, J.; Yan, H.; Liu, D. Designing Novel High-Performance Shale Inhibitors by Optimizing the Spacer Length of Imidazolium-Based Bola-Form Ionic Liquids. *Energy Fuels* **2020**, 5838−5845.

(36) Ren, Y.; Zhai, Y.; Wu, L.; Zhou, W.; Qin, H.; Wang, P. Amine- and alcohol-functionalized ionic liquids: Inhibition difference and application in water-based drilling fluids for wellbore stability. *Colloids Surf., A* **2021**, 3−9.

(37) Jia, H.; Huang, P.; Wang, Q.; Han, Y.; Wang, S.; Dai, J.; Song, J.; Zhang, F.; Yan, H.; Lv, K. Study of a gemini surface active ionic liquid 1,2-bis(3-hexylimidazolium-1-yl) ethane bromide as a high performance shale inhibitor and inhibition mechanism. *Mol. Liquids* **2020**, 3−7.

(38) Luo, Z.; Wang, L.; Yu, P. Experimental study on the application of an ionic liquid as a shale inhibitor and inhibitive mechanism. *Appl. Clay Sci.* **2017**, 267−274.

(39) Ofei, T. N.; Bavoh, C. B.; Rashidi, A. B. Insight into ionic liquid as potential drilling mud additive for high temperature wells. *Mol Liquids* **2017**, 931−939.

(40) Yang, L.; Jiang, G.; Shi, Y.; Yang, X. Application of Ionic Liquid and Polymeric Ionic Liquid as Shale Hydration Inhibitors. *Energy Fuels* **2017**, *31*, 4308−4317.

(41) Yang, L.; Kong, D.; Chang, X.; Jiang, G.; Ao, T.; Xie, C.; Kinkeyi Moukoko, A. D.; Ma, J. Counterion-specific shale hydration inhibiting performance of vinylimdazolium ionic liquids. *J. Mol. Liq.* **2021**, *335*, No. 116544.

(42) He, J.; Chen, Q.; Zhao, W.; Chen, F.; Wang, W. Hydrophobically modified cationic oligoacrylamide as a potential shale hydration inhibitor in water-based drilling fluid and mechanism study. *J. Nat. Gas Sci. Eng.* **2020**, *81*, 6−7.

(43) Xu, R.; Wu, C.; Xu, H. Particle size and zeta potential of carbon black in liquid media. *Carbon* **2007**, *45*, 2806−2809.