

**Evaluation of New Flowback Formulation for
Hydraulically Fractured Tight Gas Wells**

BY

AHMED MOHAMED

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This thesis, written by **Ahmed Essam Hassan Mohamed** under the direction of his thesis advisor and approved by his thesis committee, has been presented and accepted by the Dean of Graduate Studies, in partial fulfillment of the requirements for the degree of **MASTER OF SCIENCE IN PETROLEUM ENGINEERING**.



Dr. Dhafer A. Al Shehri
Department Chairman



Prof. Suliman Al-Homidan
Dean of Graduate Studies

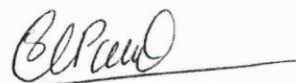
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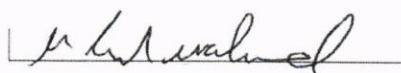
Dr. Ahmed Farid Ibrahim
(Advisor)



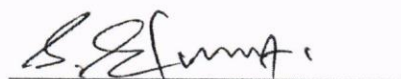
Dr. Khaled Ibrahim
(Co-Advisor)



Prof. Shirish Patil
(Member)



Prof. Mohamed Mahmoud
(Member)



Dr. Sivabalan Vijayalakshmi
(Member)



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[This thesis is dedicated to my beloved parents who encouraged me to pursue a graduate degree and have been a great source of inspiration and perseverance in life great and small]

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LIST OF ABBREVIATIONS

IFT	Interfacial Tension
CMC	critical micelles concentrations
CA	contact angle
X1	1-Butyl-3-methylimidazolium chloride ionic liquid
X2	1-Hexyl-3-methylimidazolium chloride ionic liquid
X3	1-Decyl-3-methylimidazolium chloride ionic liquid
Ppm	part per million
KCl	Potassium chloride
Wt%	weight percentage
ACS	American Chemical Society
IL	Ionic Liquids
σ	Inter Facial Tension
ρ	Density Difference
ω	Rotation per Minute
R	Tube Radius
D	Diameter of Dispersed phase
γ	Surface Tension
F	Measuring Force acting on the plate
L	Perimeter of Plate
θ	Contact Angle of Plate and Liquid

ABSTRACT

Full Name : Ahmed Essam Hassan Mohamed
Thesis Title : Evaluation of New Flowback Additives for Multistage Hydraulically Fractured Shale Wells
Major Field : Petroleum Engineering
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The evaluation of environmentally friendly flowback additives for shale gas wells is of utmost importance to mitigate formation damage with hydraulic fracturing operations. After a hydraulic fracturing job is done, most of the fluid injected into the formation is lost and affects the overall deliverability of the formation. The effectiveness of the flowback additives such as surfactants is highly impacted by harsh environmental conditions such as high salinity, and high temperature, in addition to Lithology. This study aims to assess the performance and effectiveness of new environmentally friendly flowback additives at high salinities and temperatures and compare it to commercially used flowback additives.

Different experimental analyses were conducted to screen different environmental formulations (x1, x2, x3). Surface tension measurements were conducted for four different chemical formulations at different concentrations to estimate the Critical micelle concentration (CMC). A spinning drop tensiometer was then used to measure the interfacial tension for the different chemicals with crude oil. Moreover, contact angle measurements were conducted to assess the change in the rock wettability in contact with the flowback additives. For the different experiments, seawater was used as the base fracturing fluid with a salinity of 57,000 ppm and temperatures up to 90°C.

Preliminary results for surface tension measurements show similar values of surface tension as commercial flowback additives. Four different formulations were used and yielded Surface tension values varied from 30 to 45 mN/m with CMC values ranging between 0.5 to 1 gpt. The different formulations showed different IFT values with the lowest IFT value of 3 mN/m in the case of x3. In addition, contact angle measurements showed changing the rock surface to be water wet after treating the rock with the flowback additives.

The findings of this study will highlight the use of environmentally friendly formulations to improve the fractured fluid flowback, especially in harsh conditions of high temperature and high salinity where the conventional additives are not suitable. The findings will contribute to the development of more sustainable and environmentally conscious practices in hydraulic fracturing operations. Ultimately, the utilization of these additives can help minimize water blockage, formation damage impacts, and enhance the overall efficiency of tight gas formations production.

ملخص الرسالة

الاسم الكامل: أحمد عصام حسن محمد

عنوان الرسالة: تقييم مواد تحسين التدفق للاستخدام في التكسير الهيدروليكي في آبار الطفل الصفحي

التخصص: هندسة بترول

تاريخ الدرجة العلمية: 2023

تقييم مضافات إعادة التدفق صديقة للبيئة لآبار الغاز الصخري يعتبر مهم للغاية للتخفيف من الضرر الناتج عن التكسير الهيدروليكي. بعد انتهاء عملية التكسير الهيدروليكي، يتم فقدان معظم السائل المحقون في التكوين، مما يؤثر على قدرة التكوين الشاملة. يتأثر أداء مضافات إعادة التدفق مثل مواد التشحيم بشكل كبير بظروف البيئة القاسية مثل الملوحة العالية والحرارة العالية، بالإضافة إلى الطبيعة الصخرية. يهدف هذا البحث إلى تقييم أداء وفعالية مضافات إعادة التدفق الجديدة والصديقة للبيئة في ظروف ملوحة وحرارية عالية ومقارنتها بمضافات إعادة التدفق المستخدمة تجارياً.

تم إجراء تحليل تجريبي مختلف لفحص تركيبات بيئية مختلفة (x1)، x2، x3. تم إجراء قياسات التوتر السطحي لأربع تركيبات كيميائية مختلفة بتركيزات مختلفة لتقدير التركيز الحرج للميسيل (CMC). تم استخدام جهاز القطرة الدوارة لقياس التوتر بين واجهات السوائل للمواد الكيميائية المختلفة مع النفط الخام. علاوة على ذلك، تم إجراء قياسات زاوية الاتصال لتقييم تغيير تراكيب الصخور عند التماس مع مضافات إعادة التدفق. في التجارب المختلفة، تم استخدام ماء البحر كسائل تكسير أساسي بتركيز ملوحة 57,000 جزء في المليون ودرجات حرارة تصل إلى 90 درجة مئوية.

تظهر النتائج الأولية لقياسات التوتر السطحي قيمًا مماثلة لتلك الموجودة في مضافات إعادة التدفق التجارية. تم استخدام أربع تركيبات مختلفة وأسفرت قيم التوتر السطحي عن قيم تتراوح بين 30 و 45 ميلي نيوتن في المتر، مع قيم CMC تتراوح بين 0.5 و 1 جرام لكل لتر. أظهرت التركيبات المختلفة قيمًا مختلفة لتوتر واجهة السائل مع أدنى قيمة لتوتر واجهة السائل بلغت 3 ميلي نيوتن في المتر في حالة x3. بالإضافة إلى ذلك، أظهرت قياسات زاوية الاتصال تغيير سطح الصخور ليصبح مبللاً بالماء بعد معالجة الصخر بواسطة مضافات إعادة التدفق.

ستسلط نتائج هذا البحث الضوء على استخدام تركيبات صديقة للبيئة لتحسين إعادة تدفق السائل بعد التكسير الهيدروليكي، خاصة في ظروف الحرارة العالية والملوحة العالية حيث لا تكون المضافات التقليدية مناسبة. ستساهم النتائج في تطوير ممارسات أكثر

استدامة ووعي بالبيئة في عمليات التكسير الهيدروليكي. في نهاية المطاف، يمكن أن يساعد استخدام هذه المضافات في تقليل حجب الماء، وتأثيرات ضرر التكوين، وتعزيز كفاءة إنتاج الغاز الصخري بشكل عام.

CHAPTER 1

INTRODUCTION

1.1 Literature Review

Hydraulic fracturing is a process that demands the injection of substantial fluid volumes to increase reservoir pressure until rock fracturing occurs. However, a significant portion of the injected fluid remains unrecovered, impeding hydrocarbon flow in the wellbore. This issue is particularly challenging in unconventional reservoirs due to capillary forces that trap water within rock pores, hindering hydrocarbon recovery (Frieauf et al. 2010, Le et al. 2012, Agrawal and Sharma 2013, Himes et al. 2017; Lai et al. 2017). Extensive research has aimed to develop flowback additives that reduce surface and interfacial tension, facilitating water flowback into the wellbore.

Recently there have been several attempts to develop an environmentally friendly flowback additive to be included in the hydraulic fracturing fluid (Yue et al. 2016). A comprehensive criterion to select a flowback additive includes surface tension, interfacial tension, emulsion stability, core flood tests, and improved gravity drainage column (Rabie et al. 2019; Himes et al. 2017). They highlighted that a material reducing surface tension could yield poor core flooding outcomes, but specific interfacial and surface tension properties in surfactants could significantly enhance productivity.

(Galindo and Rimassa 2013) highlighted the limitations of relying solely on contact angle measurements to screen flowback materials. They used glucose derived from natural oils to conduct various tests, including surface tension, interfacial tension, contact angle, and sand-packed columns, assessing the effectiveness of chosen materials. Combining the base fluid with selected surfactants led to substantial recovery increases, with the most promising results achieved using a mixture of non-ionic alkylpolyglucoside and a non-ionic alkyl ethoxylate formulation (Galindo and Rimassa 2013).

Howard et al. (2010) contribution involved investigating capillary forces for flowback materials. They explored various materials with approximately 30 mN/m surface tension, examining wettability and rock adsorption. Results indicated a general reduction in capillary pressure, but permeability regain was not improved for cores exceeding 1 md, highlighting the importance of not relying solely on surface tension or interfacial tension results.

Cawiezel et al. (2010) tested surfactant formulations as flowback aids to be used with high-density fracturing fluids, reporting that selecting and optimizing a formulation should be based on collective measurements in terms of surface tension (ST), IFT, and contact angle (CA). The ultimate performance can then be confirmed by coreflood or packed column test rather than depending on a single parameter. The authors reported that maximizing the CA and minimizing the IFT is necessary for the maximum water recovery, noting that the best surfactant in high-density brine can differ from those optimized for fresh water or other fracturing fluids.

Zhang et al. (2012) evaluated flowback additives in high-salinity brines used for drilling and workover, showing that effective additives maintain their surface tension reduction properties, resulting in lower brine imbibition and increased water recovery (Zhang et al. 2012). Shuler et al.

(2016) discussed the use of different surfactants in "Huff-n-Puff" processes, suggesting that surfactants could gradually solubilize and mobilize oil droplets, leading to improved oil recovery, as supported by field data. Kim et al. (2016) evaluated oil recovery in Amott cells and fracturing fluid recovery using NMR techniques to select a surfactant for flowback in the Eagle Ford formation, recommending a combination of surfactants to maximize water and oil recovery. Rabie et al (2019) Provided a comprehensive review of testing methods to validate a surfactant or a microemulsion formulation for flowback use including Surface tension, interfacial tension, contact angle, and coreflood. Rajesh et al. 2021 The study addresses challenges in the full recovery of aqueous-based fluids in hydraulic fracturing, impacting water saturation, clay swelling, and permeability. Nano-emulsion-based flowback aids, featuring ester-based solvents, alcohols, and surfactants, were developed for oil-bearing sandstone and carbonate formations. These aids exhibit low surface tension (22–30 mN/m) and interfacial tension (<6 mN/m), crucial for reducing capillary pressure. Nano-emulsion particle size ranges from 5 to 15 nm, preventing emulsion formation with crude oil. Non-ionic and anionic surfactant-based formulations excel for sandstone, while non-ionic and cationic surfactant-based formulations perform better for carbonate. Column tests and core flow experiments reveal rapid aqueous fluid displacement and enhanced oil flow, increasing permeability with flowback aids. The study demonstrates the efficacy of these enhancers in promptly recovering fracturing fluid, mitigating water saturation, and boosting productivity in low permeability oil reservoirs through tailored chemical interventions.

Conventional flowback additives may exhibit reduced effectiveness under severe conditions, leading to decreased recovery rates and potential operational issues. To optimize the flowback process in these demanding environments, there is an urgent need to develop innovative ionic liquid-based flowback additives designed to withstand high temperatures and enhance fluid

recovery. The research endeavor seeks to evaluate an environmentally stable formulation designed for flowback applications, with ionic liquids offering promise as green solvents characterized by unique attributes such as non-volatility, non-flammability, chemical and thermal stability, environmental friendliness, and the ability to remain in liquid form at high temperatures (Luo et al. 2017, Rita de Cássia et al. 2018). These ionic liquids have been explored for their potential to enhance oil recovery like conventional surfactants, further enhancing well performance.

1.2 Ionic Liquids

Ambient-temperature liquid salts known as ionic liquids are defined as liquids at room temperature consisting solely of ions. ILs are made by combining various organic cations and anions (**Fig. 1** and **Fig. 2**). Organic cation ILs include quaternary ammonium, phosphonium, pyridinium, and imidazolium salts. IL are characterized by a low melting point (less than 100°C), high viscosity, low vapor pressure, low toxicity, high polarity, good thermal stability, and chemical stability. ILs are categorized into eleven classes by their properties including, neutral, acidic, basic, functionalized, protic, chiral, supported, bio-ionic, polymerized, energetic ionic liquids, and those featuring amphoteric anions (Hajipour and Rafiee, 2015). Several review articles explored the realm of ionic liquids, their several applications in different fields and recent advancements in synthesis techniques (Bera and Belhaj 2016; Vekariya 2017; Nasirpour et al. 2020; Nasirpour et al. 2020; Atilhan and Aparicio 2021; Hussain et al. 2023; Alade et al. 2023; Song et al. 2023).

The superior interfacial activity of ILs at the oil-water interface arises from their unique molecular structure. ILs consist entirely of ions, which allows them to have both hydrophobic and hydrophilic components within a single molecule. This amphiphilic nature enables ILs to strongly adsorb and orient themselves at the hydrocarbon/water interface due to the affinity of their charged components to each phase. The ability of ILs to form a stable and robust interfacial layer stems

from the arrangement of ions at the interface, creating a barrier that reduces interfacial tension between oil and water. Additionally, the tunability of ILs, achieved by altering their cation or anion components, allows for customization of their interfacial properties, making them highly effective in various applications such as ILs-assisted EOR, demulsification, and other processes where manipulating the oil-water interface is crucial (Sakthivel et al. 2017; Song et al. 2023). The quick adsorption and spread of IL cations at the hydrocarbon/water interface was behind the reduction of the dynamic IFT between toluene and water from 36.3 mN/m to 12.8 mN/m (Jia et al. 2020). The unique combination of thermal stability, structure tunability, strong interfacial activity, and reduced environmental impact positions ILs as promising candidates for replacing surfactants in various petroleum production operations, especially in challenging conditions involving high salinity and temperature.

Conventional flowback additives may exhibit reduced effectiveness under severe conditions, leading to decreased recovery rates and potential operational issues. To optimize the flowback process in these demanding environments, there is an urgent need to develop innovative ionic liquid-based flowback additives designed to withstand high temperatures and enhance fluid recovery. The research endeavor seeks to evaluate an environmentally stable formulation designed for flowback applications, with ionic liquids offering promise as green solvents characterized by unique attributes such as non-volatility, non-flammability, chemical and thermal stability, environmental friendliness, and the ability to remain in liquid form at high temperatures (Luo et al. 2017, Rita de Cássia et al. 2018). These ionic liquids have been explored for their potential to enhance oil recovery like conventional surfactants, further enhancing well performance.

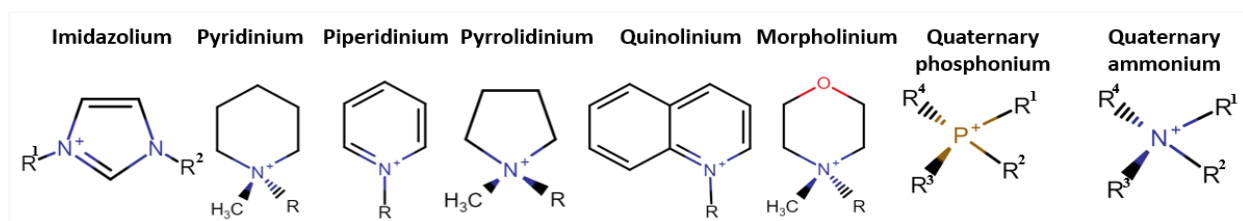


Figure 1 Different cations used to make ionic liquids

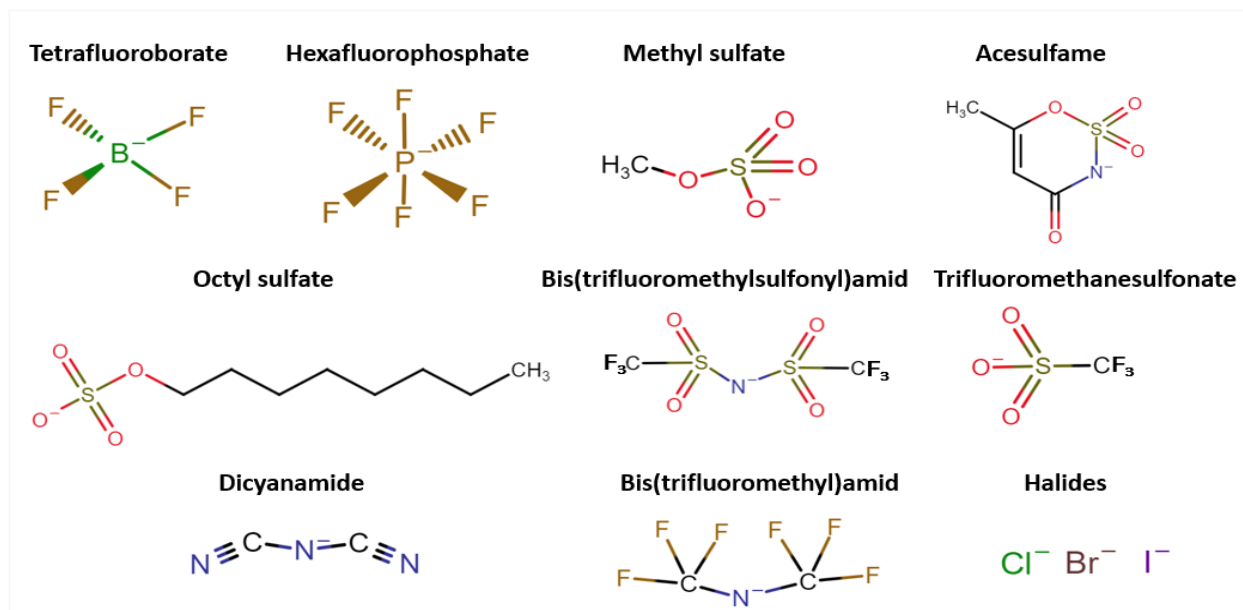


Figure 2 Different anions used to make ionic liquids

CHAPTER 2

METHODOLOGY

2.1 Material

In the current study, different salts were used to prepare the solutions representing the formation and the fracture fluids. **Table 1** summarized the salt composition for the formation brine and fracture fluids salinity. All salts utilized in the preparation of brine solutions were of ACS grade and sourced from Sigma Aldrich. To simulate natural gas flow, N₂ gas was chosen. For interfacial tension measurements, light crude oil was used.

Different methylimidazolium chloride ionic liquids were evaluated as flowback additives. **Table 2** summarizes the composition and structure of the used ionic liquids with different carbon chain lengths.

Kentucky sandstone cores with permeability of 0.1 md were used in the coreflood experiments. **Table 3** summarizes the XRD analysis for the core samples. The cores dimensions were 1.5 in. in diameter and 3 in. in length.

Ionic Species (provided)	Formation brine, ppm	Fracture base fluid, ppm
Na ⁺	59,491	18,414
K ⁺	0	577
Ca ²⁺	19,040	577
Mg ²⁺	2,439	2,040
Cl ⁻	132,060	32,031
SO ₄ ²⁻	350	5,206
HCO ₃ ⁻	354	
TDS	213,734	58,857

Table 1 The salt composition for the formation brine and fracture fluids salinity

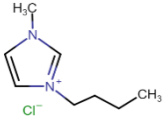
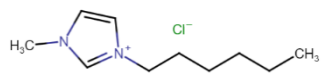
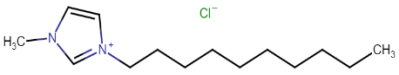
1-Butyl-3-methylimidazolium chloride	1-Hexyl-3-methylimidazolium chloride	1-Decyl-3-methylimidazolium chloride
C ₈ H ₁₅ ClN ₂	C ₁₀ H ₁₉ ClN ₂	C ₁₄ H ₂₇ ClN ₂
		

Table 2 composition and chemical structure of the ionic liquids used in the study

Mineral	Quartz	Illite	K-Feldspar	Plagioclase
Wt%	66	14	3	17

Table 3 Mineral composition of Kentucky sandstone cores used in the study

2.2 Experimental Design

Methodology for the proposed study comprises several critical steps:

2.2.1 CMC Determination and Surface Tension Analysis:

The evaluation of the Critical Micelle Concentration (CMC) for various chemicals was conducted by means of surface tension measurements. A selection of different chemicals will undergo screening to assess their effectiveness in reducing surface tension. Estimation of the CMC concentration was carried out to optimize the chemical's ideal concentration. The KRUSS K100 tensiometer will serve as the precise tool for measuring the surface tension of chemicals, including their critical micelle concentrations. **Fig 3** and **Equation 1** show the configuration and mathematical formula used by the device to measure surface tension. The device measures the value for surface tension then increases the surfactant concentration to allow for a range of surface tension measurements to be captured. All experiments were conducted under ambient conditions.

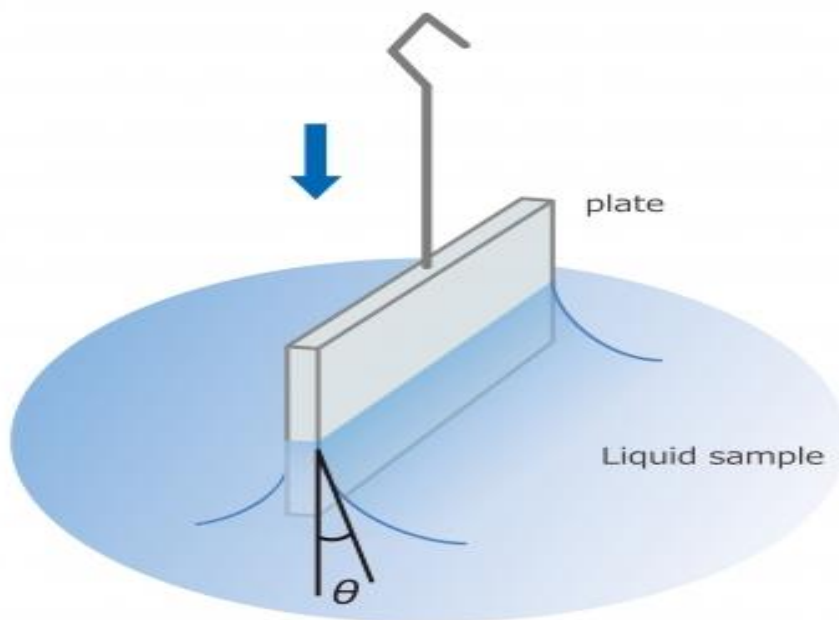


Figure 3-Surface tension measurement methodology for different ionic liquids at different concentrations to estimate the Critical micelle concentration (CMC)

$$\gamma = \frac{F}{L \cos(\theta)} \quad (1)$$

Where:

γ =Surface Tension

F = Measuring force acting on the plate

L = Perimeter of plate

θ = Contact angle between plate and liquid

2.2.2 Interfacial Tension (IFT)

This task entails the measurement of interfacial tension and wettability to explore the influence of flowback additives on the wettability characteristics of tight rock formations and the interfacial tension between the hydraulic fracturing fluid and the hydrocarbon fluids within the formation. The KRUSS spinning drop tensiometer was utilized to measure IFT. This instrument is capable of assessing IFT under different temperature conditions and a range of spinning speeds. IFT was measured at different temperatures values up to 90°C. light crude oil was chosen along with the chosen surfactants. **Fig 4** and **Equation 2** show the concept and formula for the device.

$$\sigma = \frac{\Delta\rho\omega^2 R^3}{4} \quad 2$$

Where:

σ = Inter Facial Tension

$\Delta\rho$ = density difference between the two phases

ω = rotation per minute

R = tube radius

d = diameter of Dispersed phase

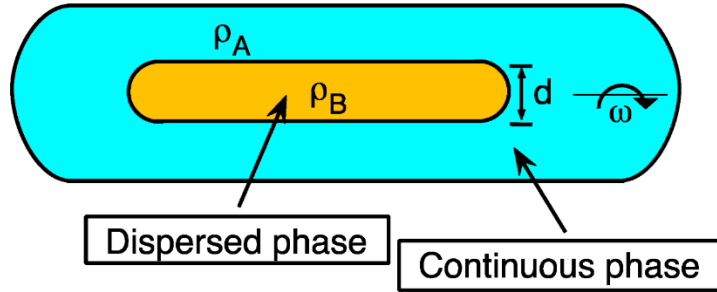


Figure 4 -Surface tension measurement methodology between Light crude oil and chosen formulation.

2.2.3 Wettability measurements

The assessment of the impact of ionic liquids on rock wettability was conducted through contact angle measurements using the sessile drop method and a drop shape analyzer. Insights into how ionic liquids influence rock wettability were obtained through this method. Contact angle was conducted on pure quartz slides pretreated with formation brine. Two different quartz samples were firstly pretreated in the formation brine to mimic the initial conditions of the formation behavior. The first sample was used to test the wettability behavior of the fracturing fluid droplet on the rock surface without the presence of ionic liquids were measured with N₂ is the surrounding phase. The same experiment was repeated on the second sample with fracturing fluid droplet includes ionic liquid and flowback aids. The conditions for the experiments were 100 psi and 50C.

Fig 5 shows the device used for taking contact angle measurements.



Figure 5- Drop shape analyzer used for contact angle measurements

2.2.4 Regain Permeability Measurements

Two sets of coreflood experiments were performed using tight Kentucky sandstone cores with permeability of 0.1 md to evaluate the effectiveness of flowback additives in regaining the formation permeability after the hydraulic fracturing process. **Fig. 6** summarizes the core flood process used to evaluate the performance of the ionic liquids to regain the hydrocarbon permeability and unloading the fracture fluids. The cores were dried at 90°C and the dry weight was estimated, and the cores porosity was estimated with gas porosimeter. The cores were then saturated under vacuum with the formation brine. The initial cores permeability was calculated through coreflood with formation brine injection at 0.5 cm³/min until stabilized pressure

conditions. The saturated weight was then estimated to calculate the cores porosity, in addition NMR was conducted to estimate the water volume and distribution inside the cores.

The first drainage step was then followed where the N_2 was injected from the outlet to the inlet direction at 5 cm³/min until pressure stabilization and no more water production. The irreducible water saturation ($S_{W_{irr1}}$) was estimated through the volumetric method as a function of the cores weight and then validated with NMR measurements. Finally, the effective gas permeability (K_{g1}) was calculated at the irreducible water saturation.

To mimic the fracturing fluid leaks to the formation during the fracturing process, the fracture fluid was injected into the cores from the inlet to the outlet direction until pressure stabilization. Similarly, the water saturation was estimated through volumetric calculations and validated with the NMR measurements. The effective water permeability at the residual gas saturation was calculated.

The final step was the flowback process, where the N_2 was injected in the reverse direction similar to the first drainage process until pressure stabilization and no more water production is observed. The irreducible water was then estimated ($S_{W_{irr2}}$) and the final effective gas permeability (K_{g2}) was calculated.

The regain percentage in the gas permeability was calculated as follows, $(K_{g1} - K_{g1})/K_{g1}$. In addition, the percentage of flowback recovery was calculated as a function of the irreducible water saturation after N_2 injection stages.

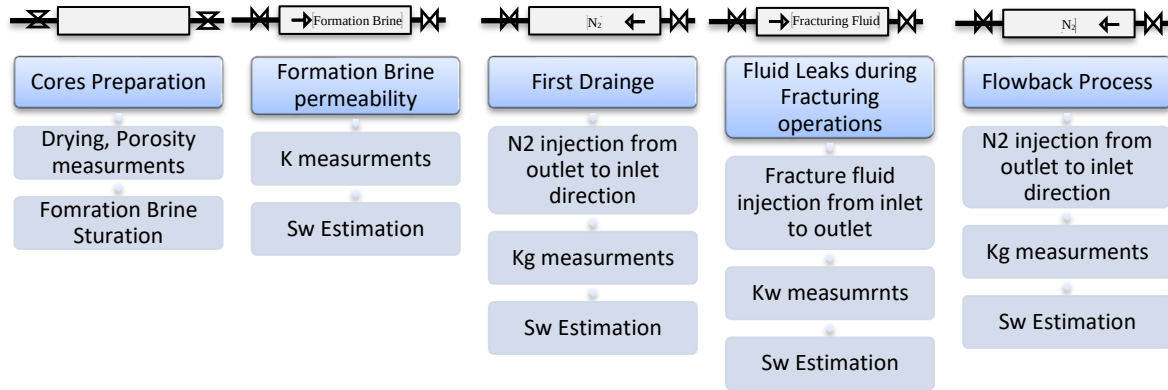


Figure 6 Coreflood workflow procedures conducted to test the regain permeability and the flowback recovery

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Surface Tension and CMC Measurements Results

The surface tension measurements were conducted using two different brine solutions to examine the impact of salinity type and composition on the ionic liquids' behavior. 5 wt% KCl brine was first tested, and then the results were compared with the fracture fluid base as highlighted in **Table 1**.

Fig. 7 illustrates the relationship between surface tension and the concentration of three different ionic liquids prepared in 5wt% KCl brine. As the concentration of these ionic liquids increases, there is a notable decrease in surface tension until it reaches a stabilized value, which is typically referred to as the Critical Micelle Concentration (CMC). Furthermore, **Fig.7** also demonstrates the impact of varying carbon chain lengths within the ionic liquids. Specifically, it shows that as the carbon chain length increases from ionic liquid X1 to X3, there is a significant reduction in surface tension. The stabilized surface tension values are observed to be 47 mN/m for X1, 44 mN/m for X2, and 39 mN/m for X3, respectively.

Significantly, the Critical Micelle Concentration (CMC) values exhibit a discernible decrease concomitant with the incremental carbon chain length of the ionic liquids under investigation. Specifically, the CMC values are quantified at 700 ppm for X1, 500 ppm for X2, and 300 ppm for X3. This elucidation underscores the intricate relationship between the concentration of ionic liquids, the extension of their carbon chains, and their consequential impact on surface tension and CMC values. These meticulous measurements provide substantive insights into the nuanced behavior of these compounds. The observed reduction in CMC values with an augmented carbon chain length implies an enhanced efficacy of ionic liquids with longer carbon chains in mitigating surface tension. This analytical revelation holds notable significance, offering a deeper understanding of how molecular attributes, particularly carbon chain length, dictate the capacity of these substances to form micelles and influence surface tension. Such insights bear relevance in diverse applications, particularly those wherein the modulation of surface tension is of paramount importance, such as in industrial processes or environmental assessments.

Fig. 8 presents Surface tension as a function of ionic liquid concentrations for three distinct ionic liquids, specifically focusing on their performance in a fracturing fluid base. This figure essentially replicates **Fig. 7** but within the context of ionic liquids used in a fracturing fluid, aiming to investigate how different ions impact the behavior of these ionic liquids.

Similarly, the effect of the carbon chain length on the behavior of the ionic liquids remains consistent. As the chain length increases, there is a noticeable reduction in surface tension values. An intriguing observation in this figure is the influence of additional ions, aside from KCl, in the brine. The introduction of these different ions appears to enhance the performance of the ionic liquids. In this context, the stabilized surface tension values were recorded at 42.5 mN/m for x1, 41.3 mN/m for x2, and 39 mN/m for x3, respectively. Consequently, the surface tension values decrease when different ions are present, aligning with the results obtained from the literature review, which indicated that ionic liquids performed better in the presence of divalent ions (Lashkarbolooki et al. 2018). This figure provides valuable insights into how various ions can affect the behavior of ionic liquids within a fracturing fluid, shedding light on their potential applications and optimization in hydraulic fracturing processes.

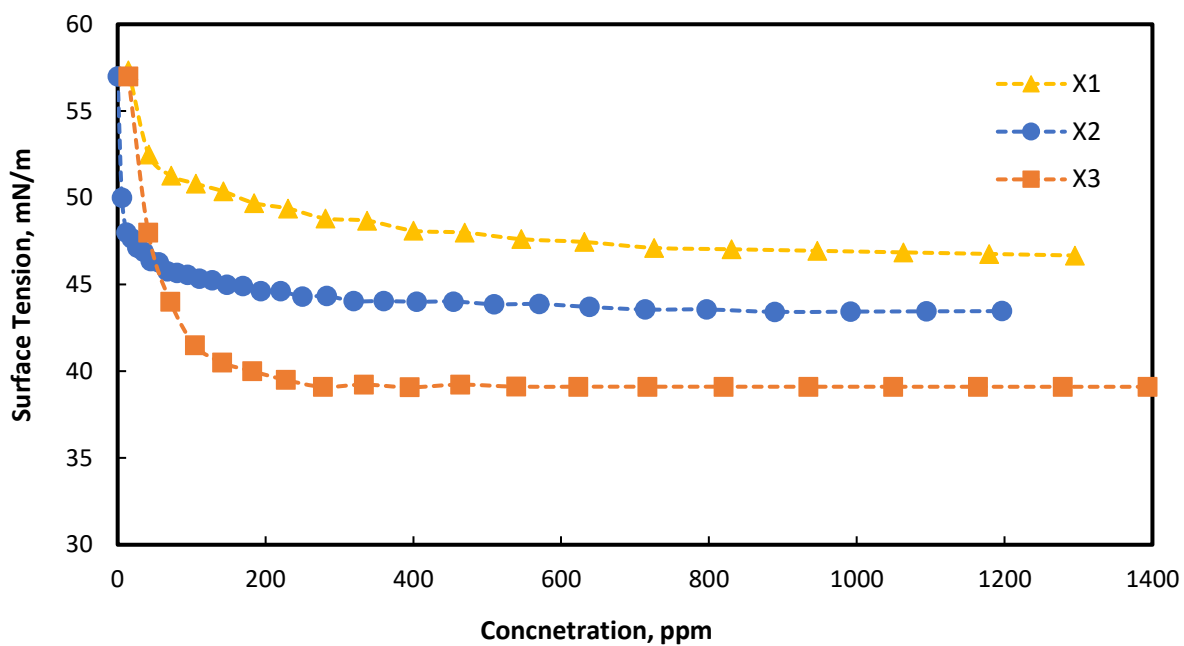


Figure 7 Surface tension as function of ionic liquid concentrations for the three different ionic liquids in 5wt% KCl

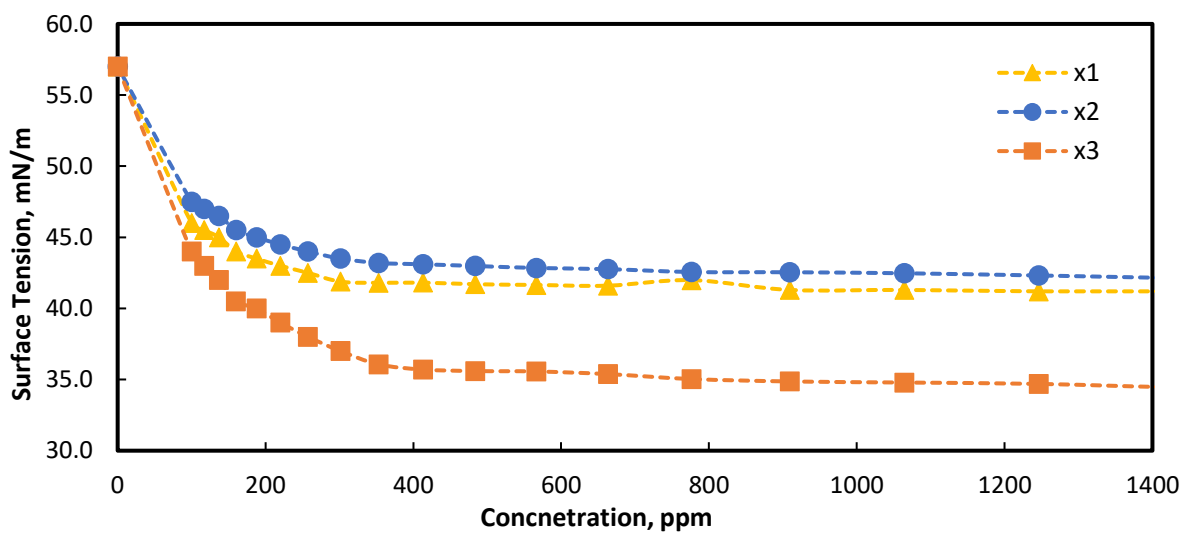


Figure 8 Surface tension as function of ionic liquid concentrations for the three different ionic liquids in fracturing fluid base.

The CMC values exhibit a discernible decrease concomitant with the incremental carbon chain length of the ionic liquids under investigation. Specifically, the CMC values are quantified at 1000 ppm for X1, 600 ppm for X2, and 400 ppm for X3. This elucidation underscores the intricate relationship between the concentration of ionic liquids, the extension of their carbon chains, and their consequential impact on surface tension and CMC values. It is clear that the increase of alkyl-chain length in the ILs head group decreases both the surface tension as well the overall CMC of the system. Similar responses were observed in previous studies as well. (Sakthivel, Chhotaray, et al., 2015; Sakthivel, Velusamy, et al., 2015; Sakthivel & Babu Salin, 2021; Velusamy et al., 2017), which implies that the increase of chain length in the ILs experienced the increase of van der Waals forces (hydrophobic interactions) that exist between the ILs units (Smit et al., 1990) and that result in for the early aggregation or micellar formation for the lengthier chain containing ILs than the shorter chain ones. As well, their exceptional assembly at the interfacial system yields for the early saturation and better reduction in the surface tension that in fact helps to lower the CMC values. These meticulous measurements provide substantive insights into the nuanced behavior of these compounds. The observed reduction in CMC values with an augmented carbon chain length implies an enhanced efficacy of ionic liquids with longer carbon chains in mitigating surface tension. This analytical revelation holds notable significance, offering a deeper understanding of how molecular attributes, particularly carbon chain length, dictate the capacity of these substances to form micelles and influence surface tension. Such insights bear relevance in diverse applications, particularly those wherein the modulation of surface tension is of paramount importance, such as in industrial processes or environmental assessments.

3.2 IFT Measurements Results

Based on surface tension measurements, X3 showed the highest performance and lower surface tension values with lower CMC values. Hence, the rest of the experimental investigation was applied on X3.

IFT was measured using a spin drop tensiometer for X3 at different concentrations of 0.5 and 1 gpt, in different salt compositions. **Fig. 9** illustrates IFT results with 0.5 gpt of ionic liquid X3 in a 5 wt% KCl solution. These measurements were conducted at various temperatures, with a constant spinning speed of 10,000 rpm. At 50°C, the IFT initially measured 16 mN/m, gradually stabilizing at 14.5 mN/m, which is significantly lower than the IFT of 50 mN/m observed in the absence of the ionic liquid. However, there is no discernible trend in IFT with temperature, as the stabilized IFT values remain relatively constant at 14.5 mN/m, 14 mN/m, and 15 mN/m at temperatures of 50°C, 70°C, and 90°C, respectively. Similarly, **Fig. 10** displays IFT results for X3 with 0.5 gpt of ionic liquid X3 in a fracturing base fluid at various temperatures, at 10,000 rpm. the IFT in the fracturing-based fluid, which contains different salt ions, is lower compared to the IFT observed in a 5 wt% KCl brine which aligns with the surface tension observation of improved ionic liquid performance in the presence of divalent salts in the solution. At 50°C, the IFT stabilizes at 6.2 mN/m, a significant reduction from the 14.5 mN/m observed in the 5 wt% KCl solution. However, as the temperature increases, the IFT values also increase, stabilizing at 6.2 mN/m, 7 mN/m, and 8.2 mN/m at temperatures of 50°C, 70°C, and 90°C, respectively.

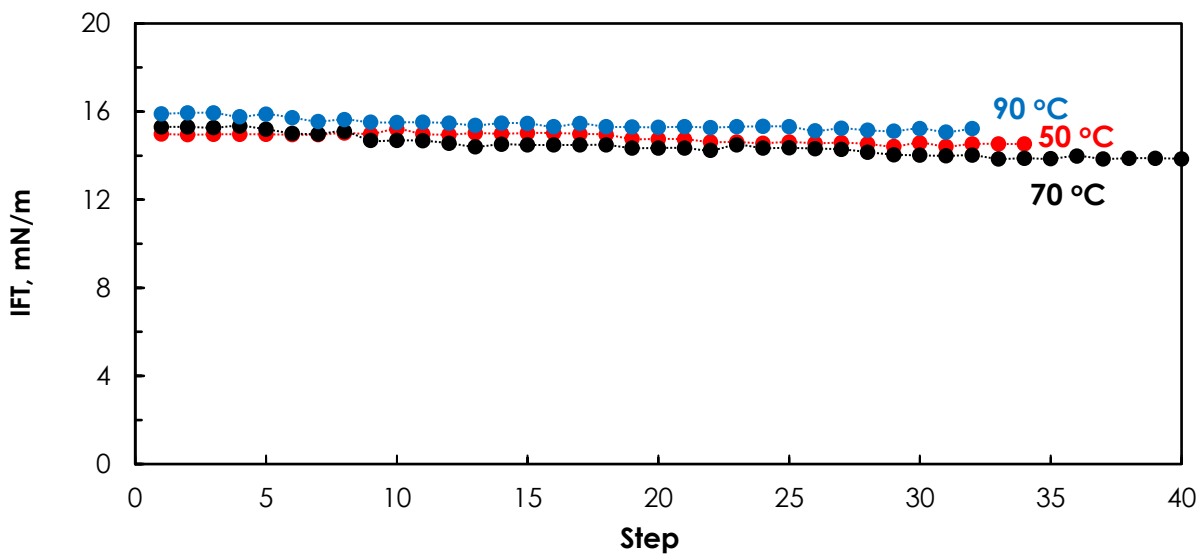


Figure 9 Spin drop tensiometer IFT results for X3 at 0.5 gpt in 5 wt% KCl at different temperatures with a spinning speed of 10000 rpm.

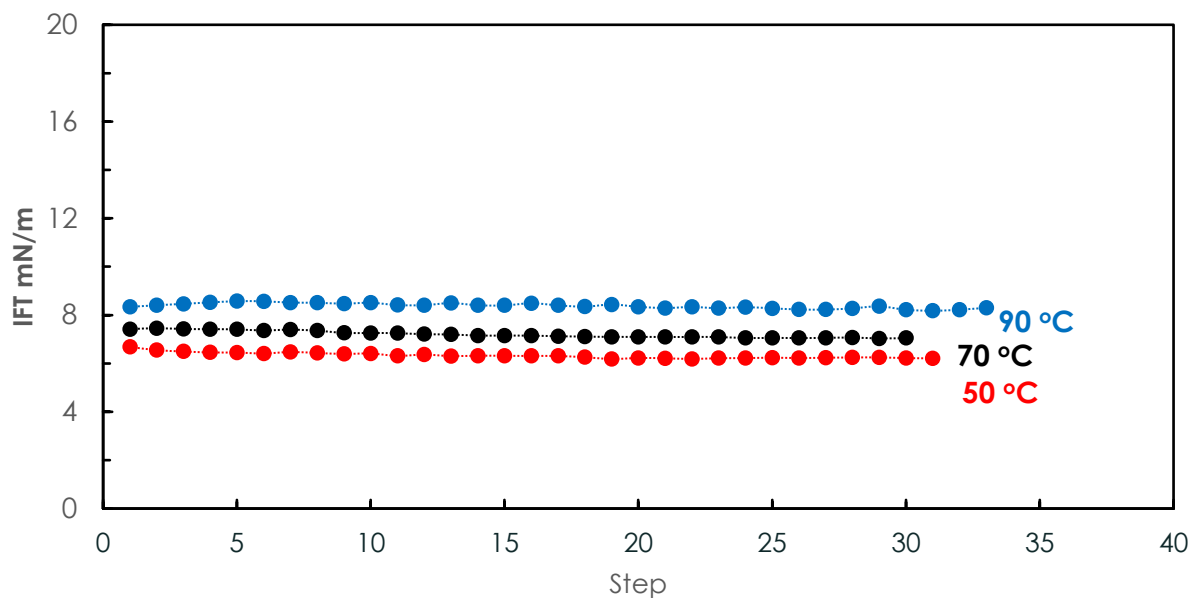


Figure 10 Spin drop tensiometer IFT results for X3 at 0.5 gpt in fracturing base fluid at different temperatures with a spinning speed of 10000 rpm.

Fig. 11 captures a comprehensive overview of IFT measurements, delving into the nuanced influences of temperature, ionic liquid concentrations, and salt composition. The graphical representation illuminates that the introduction of various ions into the brine consistently enhances the efficacy of the ionic liquid in reducing IFT, irrespective of temperature variations or the concentration of the ionic liquid.

Moreover, the figure discerns a more pronounced impact of temperature on IFT in the context of the fracturing-based fluid compared to the 5 wt% KCl solution. Specifically, in the fracturing-based fluid, IFT experiences an upward trajectory with escalating temperatures. Concurrently, the figure underscores that elevating the concentration of the ionic liquid, ranging from 0.5 to 1 gpt, engenders a reduction in IFT. This reduction is more conspicuously evident in the case of the fracturing-based fluid, accentuating the heightened sensitivity of IFT to variations in ionic liquid concentration within this specific fluid medium. These findings contribute valuable insights into the multifaceted interplay of temperature, ionic liquid concentration, and salt composition on the interfacial tension dynamics, particularly in the context of fracturing-based fluid systems.

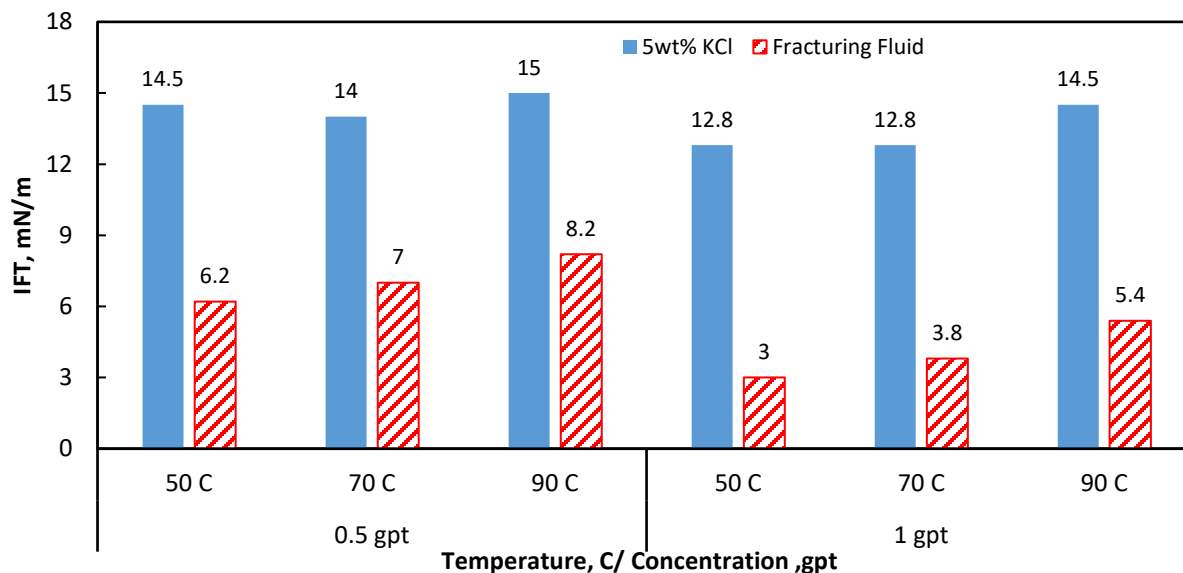


Figure 11 IFT results summary at different ionic liquid concentrations in 5 wt% KCl and Sea water, and at different temperatures

3.3 Wettability Measurements Results

The evaluation of contact angles was performed utilizing the sessile drop technique under controlled conditions of 100 psi pressure and a temperature of 50°C, as depicted in **Fig. 12** and **Fig. 13**. In this method, an ionic liquid was introduced onto a quartz surface immersed in Nitrogen gas (N₂).

The initial contact angle for 5 wt% KCl in N₂ was established at 45°. Subsequent introduction of the ionic liquid into the base fluid resulted in a discernible reduction in the contact angle, culminating in a decrease to 33°. This observed decrease in the contact angle signifies a subtle shift toward a more water-wet rock surface. The alteration in the contact angle provides valuable insights into the influence of the introduced ionic liquid on the wettability characteristics of the rock surface, suggesting a propensity for enhanced water-wetting with the incorporation of the ionic liquid into the base fluid. Among the developed flowback aids, X3 emerges as the most

effective ionic liquid in the role of a flowback additive. Notably, X3 demonstrates the lowest surface tension and interfacial tension, showcasing exceptional performance. This efficacy is particularly pronounced when considering the use of seawater as a fracturing fluid base, where the interfacial tension reaches values lower than 6 mN/m. This aligns seamlessly with the criteria established by Rajesh et al. in 2021, further validating the superior capabilities of X3 as a flowback enhancer. The ability of X3 to achieve such low interfacial tension values, especially in the challenging context of seawater-based fracturing fluids, underscores its potential significance in optimizing flowback processes and reducing the associated challenges in tight formations.

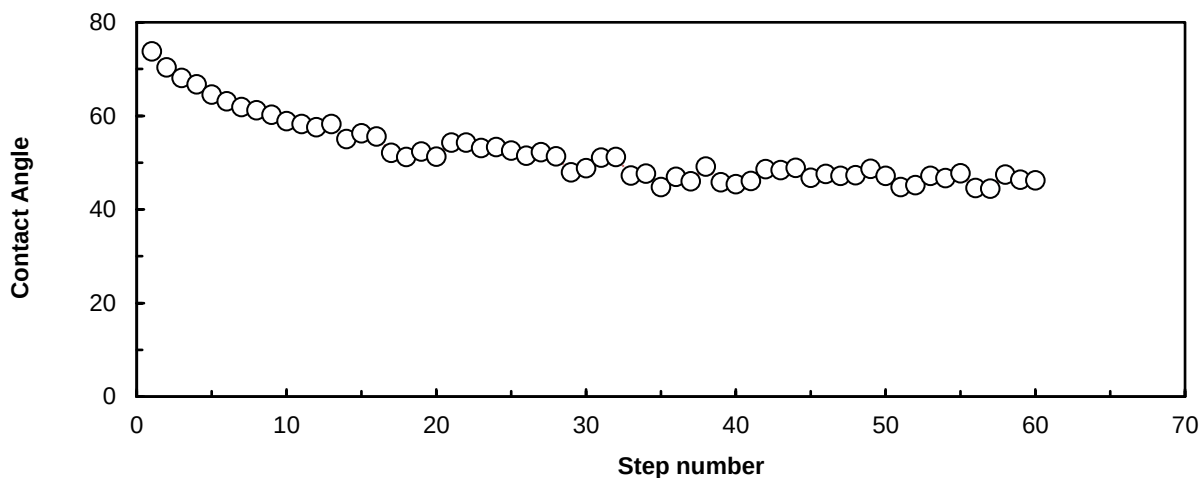


Figure 12 contact angle values for base fluid of 5 wt% KCL without ionic liquid

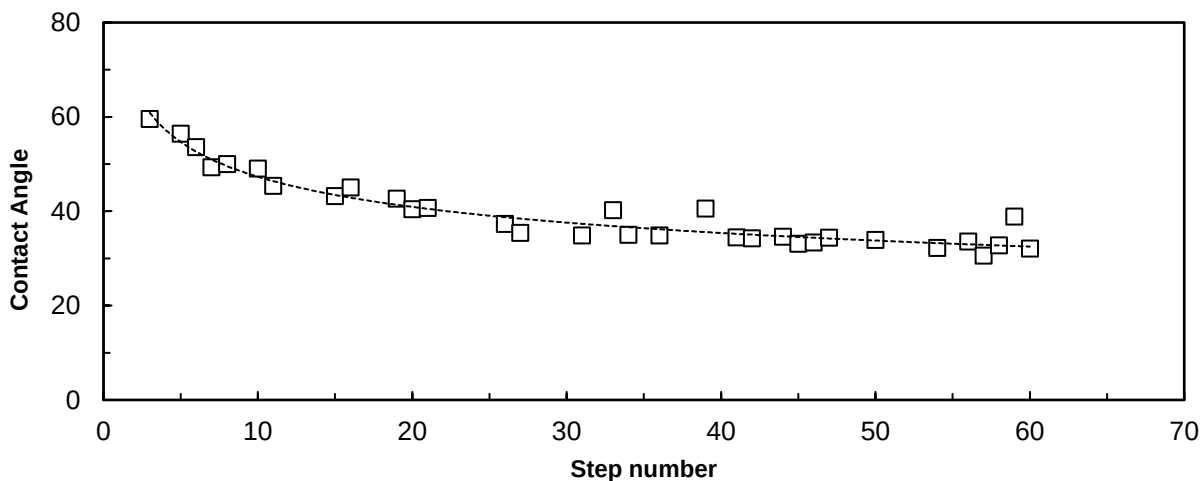


Figure 13 contact angle values for base fluid of 5 wt% KCL 0.5gpt ionic liquid

3.4 Core flood Measurements Results

Two core flood experiments were conducted following the procedures in **Fig. 14** without (core_1) and with (core_2) adding the ionic liquid to the fracturing fluids. **Table 4** Summarizes the initial preparation results for the two cores. The cores porosity was found to be 0.17, and 0.16 for core_1, and 2, respectively, with initial water permeability of 0.14 and 0.09 md.

Core	Length, in.	Diameter, in.	Porosity, fraction	K _{wi} , md
Core_1	3	1.5	0.17	0.14
Core_2	3.2	1.5	0.16	0.09

Table 4 Dimensions and petrophysical properties of Kentucky sandstone cores used in the study

Fig. 15 presents a summary of the pressure drop across core_1 during various injection stages. In the initial stage of formation brine injection at a rate of 0.5 cm³/min, the pressure drop across the core stabilized at 600 psi, and the initial core permeability was estimated at 0.14 md. The first drainage stage persisted for over 800 minutes of N₂ injection, where the pressure stabilized at 270 psi. During this stage, K_{g1} was estimated to be 0.06 md, and S_{wr1} was calculated through volumetric considerations to be 0.58.

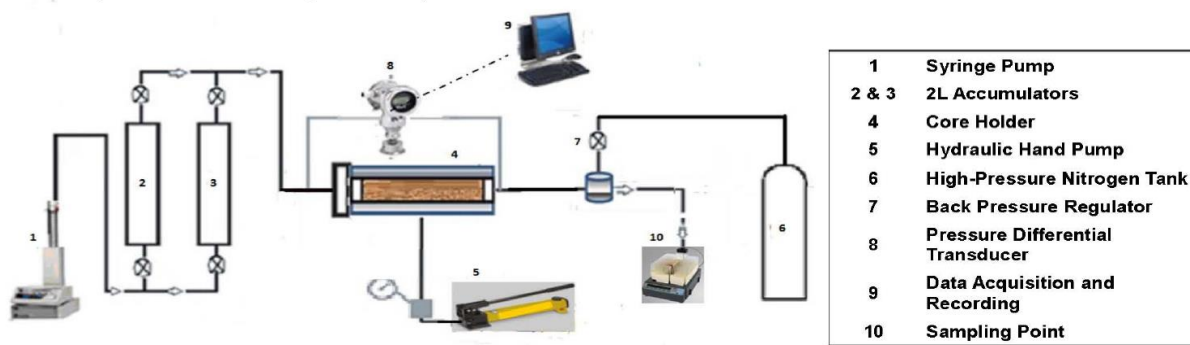


Figure 14 Core flooding system used to verify the effectiveness of the surfactant

In the third stage of fracturing fluid injection without the presence of ionic liquid, a similar initial water permeability of 0.14 md was observed, with no discernible impact on residual gas saturation. The subsequent flowback stage exhibited a higher stabilized pressure drop of 300 psi, with an estimated K_{g2} of 0.05 md and a higher irreducible water saturation of 0.61. This behavior is characteristic of tight formations after exposure to fracturing fluids with lower salinity compared to the formation's original salinity. Lower water salinity leads to a thicker double layer and a more water-wet system, resulting in higher irreducible water saturation and lower effective gas permeability. The permeability loss was determined to be 14% of its initial value, and the increase in irreducible water saturation due to retaining some of the fracturing fluid in the system was estimated to be 6%.

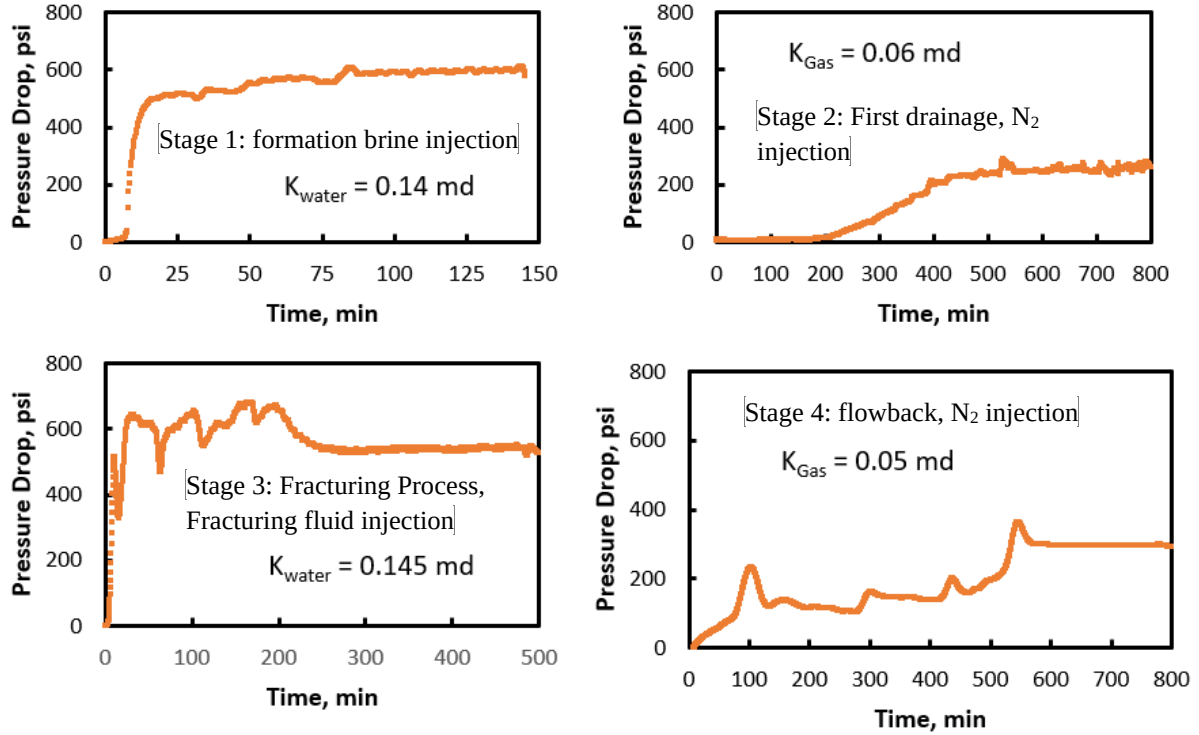


Figure 15 Pressure drop across the core for different stages of coreflood experiment 1

The water distribution within the core underwent further examination using NMR measurements. In **Fig. 16a**, the incremental porosity is depicted as a function of T2 relaxation time for various stages, including fully saturated, first drainage, and flowback stages. The figure illustrates that N_2 injection displaces water from larger pores, with most of the water retained in smaller pores. Notably, even after the flowback stage, when the core was exposed to fracturing fluids, a slightly higher amount of water remained in the larger pores. **Fig. 16b** illustrates the estimated water volume distribution along the core, revealing a nearly identical water displacement pattern in both the first drainage and flowback stages.

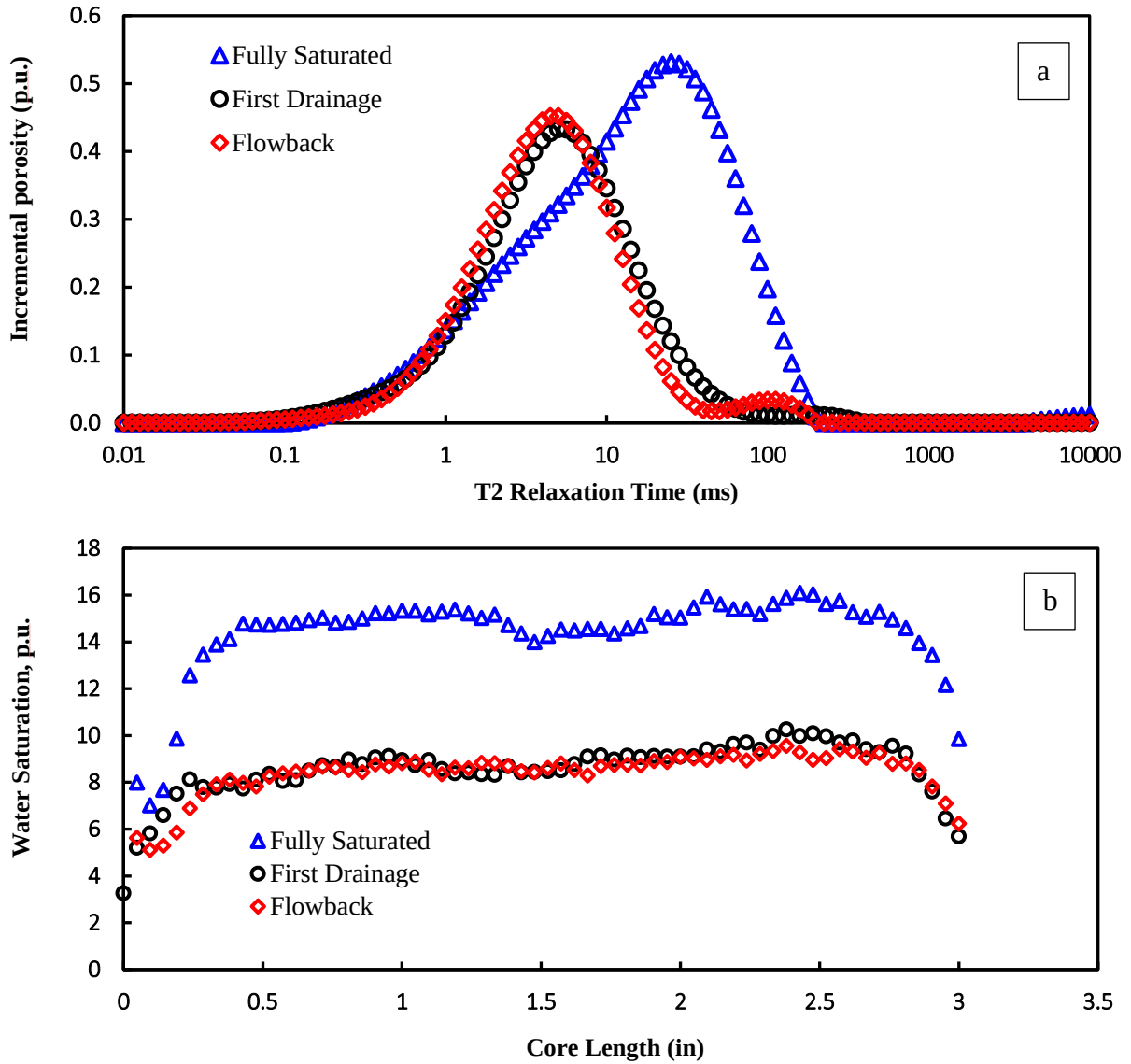


Figure 16 NMR Analysis for Core_1 without adding flowback aids, a) incremental porosity in the core versus T2 relaxation time, b) water saturation distribution at different stages.

The same procedures were replicated in Core_2, with the addition of 0.5 gpt of X3 to the fracturing fluid. **Fig. 17** provides a summary of the pressure drop across Core_2 during various injection stages. A comparable analysis was executed to assess rock permeability and water saturation. Notably, the effective gas permeability in the flowback stage exceeded that of the first drainage stage by 25%. Furthermore, a reduced irreducible water saturation was observed post-flowback

stage treatment with flowback additives, where the irreducible water saturation decreased to 0.44, marking a 21% reduction from the original value. These findings were corroborated through NMR measurements.

In **Fig. 18a**, the incremental porosity is displayed as a function of T2 relaxation time for different stages. Treating the rock with flowback aids enhanced the displacement behavior of the fracturing fluids by N₂, leading to a higher recovery of fracturing fluid during the flowback stage.

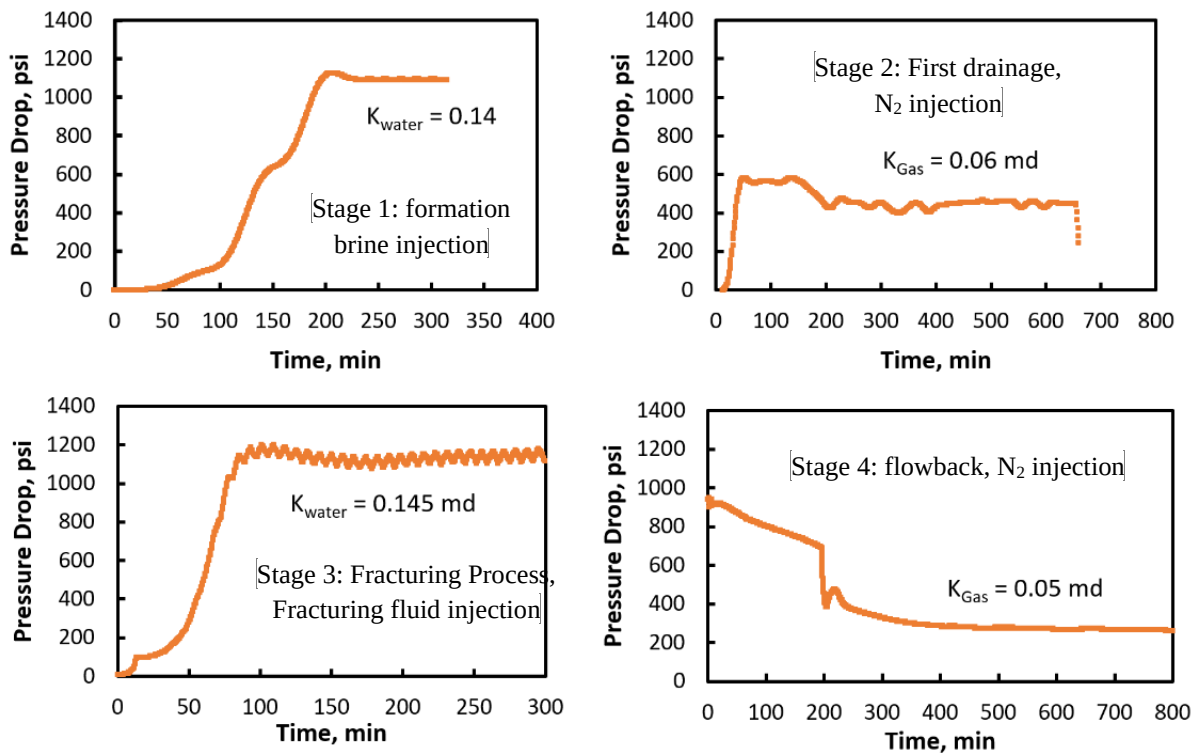


Figure 17 Pressure drop across the core for different stages of coreflood experiment 2

Fig. 18b illustrates the estimated water saturation distribution along the core, revealing greater water displacement during the flowback stage compared to the first drainage stage, consistent with volumetric calculations.

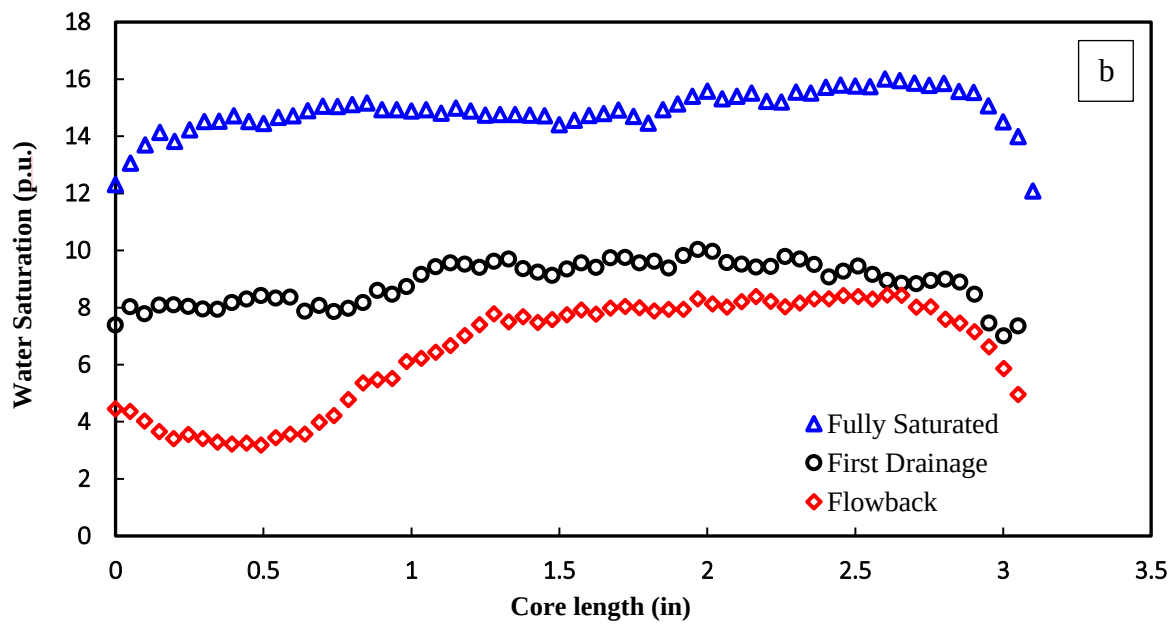
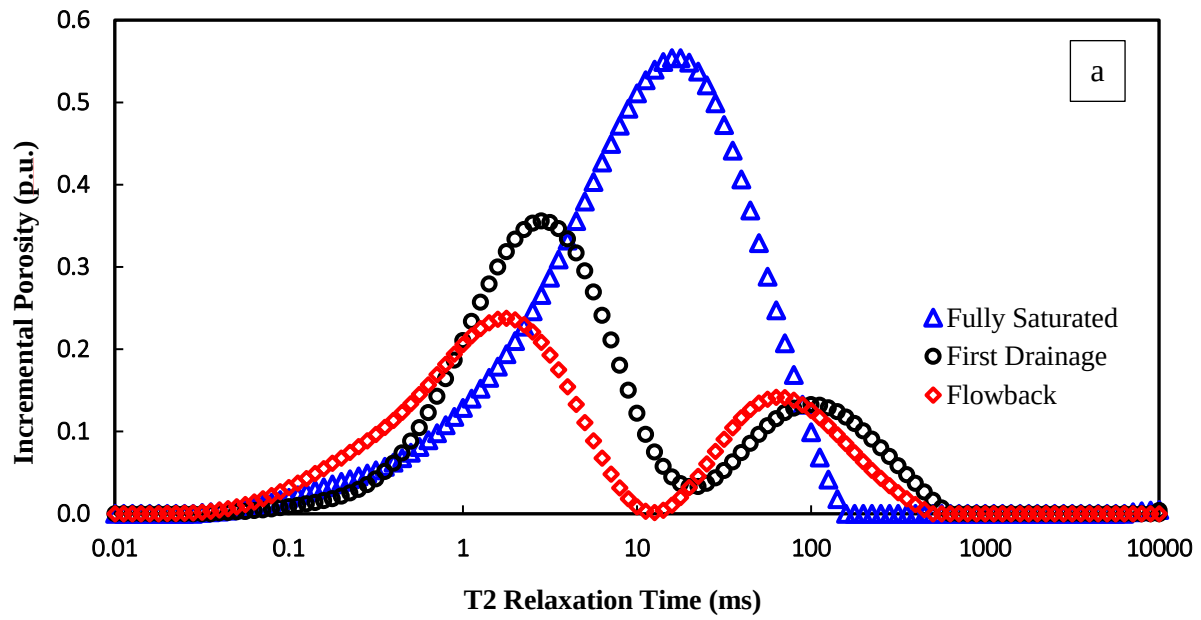


Figure 18 NMR Analysis for Core_2 with adding flowback aids a) incremental porosity in the core versus T2 relaxation time, b) water saturation distribution at different stages.

CHAPTER 4

CONCLUSIONS

This study aims to assess the performance of novel, environmentally friendly flowback additives, specifically ionic liquids, in the demanding conditions of elevated salinity and temperature encountered in hydraulic fracturing operations. Key findings with significant implications for the field have emerged:

- Surface tension measurements demonstrated the favorable surface tension reduction properties of the selected ionic liquids.
- The length of the carbon chain in the ionic liquids played a crucial role, with longer chains resulting in lower surface tension values.
- The introduction of various ions, particularly divalent ions, enhanced the performance of ionic liquids in reducing surface tension.
- Interfacial tension (IFT) measurements revealed that adding ionic liquid X3 to both 5 wt% KCl and the fracturing base fluid significantly reduced IFT compared to the absence of ionic liquid.
- Stabilized IFT values at different temperatures did not follow a predictable pattern, with temperature exerting a more pronounced effect on IFT in the case of the fracturing base fluid.

- Contact angle measurements showed that introducing ionic liquid into the base fluid shifted rock surface wettability slightly towards being more water-wet.
- The use of ionic liquids improved regained permeability by 25% compared to the base case, enhancing fracturing fluid recovery to approximately 56% of the injected volume.

These findings hold significant implications for enhancing hydraulic fracturing operations, particularly in challenging conditions characterized by high temperature and salinity, where conventional additives may fall short. Embracing environmentally friendly formulations, such as the investigated ionic liquids, can contribute to more sustainable and responsible industry practices. Ultimately, these additives have the potential to alleviate water blockage, diminish formation damage, and enhance the overall efficiency of shale gas production.

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Vitae

Name :Ahmed Essam. |

Nationality :Egyptian |

Date of Birth :6/1/1996|

Email :AhmedEssam_Mohamed@outlook.com|

Address :P.O. Box 7935-5230 58760 St,belal bin-
rabah,Dariyah,Qassim,Kingdom of Saudi Arabia.|

Academic Background :Master of Science in Petroleum Engineering, King Fahd
University of Petroleum and Minerals. Bachelors in Petroleum Engineering, King Fahd
University of Petroleum and Minerals. |