Synergetic Effect of Surfactant Concentration, Salinity, and Pressure on Adsorbed Methane in Shale at Low Pressure: An Experimental and Modeling Study

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ABSTRACT: The influence of an anionic surfactant, a cationic surfactant, and salinity on adsorbed methane (CH₄) in shale was assessed and modeled in a series of systematically designed experiments. Two cases were investigated. In case 1, the crushed Marcellus shale samples were allowed to react with anionic sodium dodecyl sulfate (SDS) and brine. In case 2, another set of crushed Marcellus shale samples were treated with cetyltrimethylammonium bromide (CTAB) and brine. The surfactant concentration and salinity of brine were varied following the Box–Behnken experimental design. CH₄ adsorption was then assessed volumetrically in the treated shale at varying pressures (1–50 bar) and a constant temperature of 30 °C using a pressure equilibrium cell. Mathematical analysis of the experimental data yielded two separate models, which expressed the amount of adsorbed CH₄ as a function of SDS/CTAB concentration, salinity, and pressure. In case 1, the highest amount of adsorbed CH₄ was about 1 mmol/g. Such an amount was achieved at 50 bar, provided that the SDS concentration is kept close to its critical micelle concentration (CMC), which is 0.2 wt %, and salinity is in the range of 0.1–20 ppt. However, in case 2, the maximum amount of adsorbed CH₄ was just 0.3 mmol/g. This value was obtained at 50 bar and high salinity (∼75 ppt) when the CTAB concentration was above the CMC (>0.029 wt %). The findings provide researchers with insights that can help in optimizing the ratio of salinity and surfactant concentration used in shale gas fracturing fluid.

1. INTRODUCTION

There have been growing interest in the development of shale gas reservoirs over the past 3 decades.¹ Shale gas is perceived as a fuel that marks a transition from high-carbon to low-carbon energy resources.²,³ However, the ultralow permeability of gas shales precludes exploiting such reservoirs through conventional production methods.⁴,⁵ The combination of hydraulic fracturing and horizontal drilling technologies has been proven to be feasible and effective for enhancing gas production from shale.¹⁰,¹¹ Hydraulic fracturing aims at promoting the permeability of shale gas reservoirs by injecting a large volume of fracturing fluid down a well at a suitable rate and pressure. The resulting fracture networks within shale are typically kept open with proppants to allow the gas flow from shale to the producing well.⁶ Water-based fluids such as slickwater and polymer-based fluids are commonly used for hydraulic fracturing in shale. Such fluids are generally composed of water (~99.5%), proppants, and a mixture of chemical additives that vary depending on the characteristics of the shale reservoir. Despite its substantial economic potential, there are still significant technical and environmental issues associated with shale gas production using water-based fracturing fluids or slickwater.

Shale swelling is one of the main technical concerns associated with the use of water-based hydraulic fracturing fluids.⁹ It is also known that water-based fracturing fluids consume a substantial amount of freshwater, which endangers drinking water resources. Besides, the various types of chemical additives that are tailored within the composition of water-based fracturing fluids necessitate a great deal of disposals for the recovered water.¹⁰,¹¹ The technical and environmental issues associated with the use of water-based fluids for hydraulic fracturing in shale motivated researchers to develop effective waterless fracturing fluid alternatives.¹²–¹⁴ Among the available options are foam-based fluids that have attracted more attention recently.¹⁴–¹⁶ Foam in porous media is as dispersions of gas in liquid. The liquid phase is continuous, while the continuity of the gas

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phase is disturbed by the existence of thin liquid films called “lamellae”.\(^{16}\) Commonly, surfactants are used as foaming agents to increase the foam stability and viscosity and reduce the surface tension. The term “surfactant” refers to a surface-active agent that has the potential to get adsorbed onto a surface or an interface. In their chemical structure, surfactants contain both a hydrophilic head and a hydrophobic region or tail.\(^{17,18}\) At liquid—gas interfaces, surfactants align themselves in such a way that their hydrophilic head is in the aqueous phase and the hydrophobic tail extrudes into the gaseous phase. This orientation allows forming a stable foam and prevents or delays coalescence.\(^{12,15}\) Surfactant-stabilized foam was reported to be a promising fracturing fluid alternative for unconventional resources, i.e., gas shales.\(^{6,19}\) Foam-based fracturing fluids consume less amount of water (5−30% of water)\(^{20}\) as compared to water-based fluids that contain up to 99% water.\(^{8}\) The lower water content produces an insignificant amount of wastewater, hence reducing the destructive impacts on the environment.\(^{20}\) Apart from reducing environmental footprints, foam-based fracturing fluids have a better proppant-carrying capacity than water-based fluids that allow efficient distribution of proppants in the fractures.\(^{7}\) The proppants’ settling velocity in the foam is about 85% lower than that in water due to the lower viscosity of water compared to foam.\(^{21}\) Other advantages of foam-based fracturing fluids include low fluid loss, low formation damage, and reduced flowback time.\(^{22}\)

There are three modes of shale gas occurrence in shales, including adsorbed gas, free gas, and dissolved gas, among which adsorbed gas makes up the most significant portion (up to 85%).\(^{23}\) It is essential to understand the interaction between fracturing fluid and gas stored within the shale matrix. Such an interaction has been widely explored for water-based fracturing fluid.\(^{11}\) Besides, the shortage of clean water in some areas urges to assess the suitability of high-salinity foam-based fluids. During the hydraulic process of shale using foam-based fluids, an interaction occurs between shale and the fracturing fluid that contains surfactants as foaming agents. Anionic and cationic surfactants are known to have the potential of significantly influencing the wetting characteristics of surfaces. Such a change in the wetting characteristics of shale could affect gas flow and ultimately influence gas recovery. Many studies have explored the role of surfactants in the development of shale gas in various contexts including but not limited to fluid immiscibility,\(^{24−26}\) hydration,\(^{27,28}\) wettability alteration,\(^{29,30}\) and gas adsorption.\(^{8}\) However, little is known about the interaction between foam-based fracturing and CH\(_4\) stored within the shale matrix. Some studies were conducted to infer such an influence on gas adsorption in shale.\(^{31−33}\) However, to the best of our knowledge, the existing studies are based on one-factor-at-a-time (OFAT) methods, which fall short in capturing and modeling the simultaneous effects of variables such as salinity, surfactant concentration, and pressure.

This study aims to experiment and model the combined effect of salinity and surfactant concentration at varying pressures on CH\(_4\) adsorption in Marcellus shale through a series of experiments that utilized the design of experiments (DOEs). Two commonly used surfactants, sodium dodecyl sulfate (SDS) (an anionic surfactant) and cetyltrimethylammonium bromide (CTAB) (a cationic surfactant), were used for the treatment of Marcellus shale samples. The influences of each surfactant at different concentrations, pressures, and salinities were examined. For a given surfactant, the concentration was varied over a wide range below critical micelle concentration (CMC) to above CMC. The salinity of the liquid phase was varied across a wide range (0.1−75 ppt) to cover salinities of freshwater, brackish water, seawater, and brine. The pressure was varied from 1 to 50 bar, while the temperature used was held constant (30 °C) throughout the experiments. The results of the experiments were then modeled, and two new mathematical models were introduced, which relate the influence of surfactant concentration, salinity, and pressure on CH\(_4\) adsorption.

### 2. RESULTS AND DISCUSSION

#### 2.1. Surfactant CMC Determination.
The CMCs of the two surfactants were obtained following the UV−vis spectroscopy method. The reader is advised to refer to ref 34 for more details.\(^{34}\) The surfactant CMC was taken as the concentration that corresponds to a sudden change in the linear relationship between the light absorbance and the surfactant concentration. The values of CMCs are 0.2 wt % for SDS and 0.029 wt % for CTAB. The CMCs are in-line with the values from the literature (e.g., CMCs of SDS and CTAB are 0.203 and 0.0022 wt % using the conductivity method, respectively,\(^{35}\) whereas the CMC of SDS is 0.008 mol/L (equivalent to 0.26 wt %) determined by the surface tension method (lowest surface tension corresponds to the CMC)\(^{36}\) and the CMC of CTAB is 0.02 wt % by the surface tension method (lowest surface tension corresponds to the CMC).\(^{57)}\)

#### 2.2. X-ray Fluorescence (XRF) Analysis.
The major, minor, and trace elements present in the shale sample were quantified by performing X-ray fluorescence (XRF) analysis. The measurements were repeated in three replicate sub-samples. As presented in Table 1, the shale sample contains a high percentage (∼57%) of silicon oxide (SiO\(_2\)), which is the main component of quartz. The high abundance of siliceous components, such as quartz, is associated with a negative charge on its surface.\(^{38}\)

### 2.3. Design of Experiment (DOE).

With the advances in data analysis, the DOE has become a powerful tool to assess experimental data. Its results can even be enhanced using techniques such as artificial neural networks,\(^{39}\) and some solid approaches can also be used to reconstruct if there is missing

| replicate | #1     | #2     | #3     | average |
|----------|--------|--------|--------|---------|
| SiO\(_2\) (%) | 56.62 | 56.62  | 58.42  | 56.56   | 57.2   |
| Al\(_2\)O\(_3\) (%) | 56.62 | 56.62  | 58.42  | 56.42   | 57.2   |
| Fe\(_2\)O\(_3\) (%) | 56.62 | 62.07  | 38.42  | 56.42   | 57.2   |
| MgO (%)   | 56.62 | 58.42  | 56.42  | 56.42   | 57.2   |
| CaO (%)   | 56.62 | 58.42  | 56.42  | 56.42   | 57.2   |
| Na\(_2\)O (%) | 56.62 | 62.07  | 52.42  | 56.42   | 57.2   |
| K\(_2\)O (%) | 56.62 | 58.42  | 56.42  | 56.42   | 57.2   |
| TiO\(_2\) (%) | 56.62 | 58.42  | 56.42  | 56.42   | 57.2   |
| P\(_2\)O\(_5\) (%) | 56.62 | 58.42  | 56.42  | 56.42   | 57.2   |
| MnO (%)   | 56.62 | 58.42  | 56.42  | 56.42   | 57.2   |
| Cr\(_2\)O\(_3\) (%) | 56.62 | 62.07  | 52.42  | 56.42   | 57.2   |
| Ni (PPM)  | 56.62 | 58.42  | 56.42  | 56.42   | 57.2   |
| Sc (PPM)  | 56.62 | 58.42  | 56.42  | 56.42   | 57.2   |
| LOI (%)   | 56.62 | 58.42  | 56.42  | 56.42   | 57.2   |
| sum       | 99.91 | 99.85  | 99.83  | 99.83   | 57.2   |
information. In this research, Box–Behnken experimental design was adopted to evaluate the effects of independent variables on the CH₄ adsorption in Marcellus shale. The studied variables in this study were surfactant concentration, salinity, and pressure denoted as C, S, and P, respectively. Two cases were studied by using SDS (an anionic surfactant) in case 1, while CTAB (a cationic surfactant) was used in case 2. Table 2 outlines the design points of the three factors in case 1, while Figure 1 shows a geometrical representation of the Box–Behnken design.

Table 2. Box–Behnken Design Points for Three Factors

| run  | P     | C     | S     | P     | C     | S     |
|------|-------|-------|-------|-------|-------|-------|
| 1    | −1    | 0     | +1    | 0     | 0     | 0     |
| 2    | +1    | −1    | 0     | 0     | 0     | 0     |
| 3    | 0     | −1    | 0.1   | 0     | −1    | +1    |
| 4    | 0     | 0     | 0     | +1    | 0     | +1    |
| 5    | +1    | 0     | +1    | +1    | +1    | 0     |
| 6    | 0     | 0     | 0     | −1    | 0     | −1    |
| 7    | 0     | +1    | +1    | 0     | +1    | +1    |
| 8    | +1    | 0     | 0.1   | 0     | +1    | −1    |
| 9    | +1    | +1    | 0     | −1    | −1    | 0     |
| 10   | −1    | +1    | 0     | 0     | 0     | 0     |
| 11   | 0     | −1    | +1    | 0     | −1    | −1    |
| 12   | −1    | 0     | 0.1   | −1    | +1    | 0     |
| 13   | 0     | +1    | 0.1   | +1    | −1    | 0     |
| 14   | 0     | 0     | 0     | −1    | 0     | +1    |
| 15   | −1    | −1    | 0     | +1    | 0     | −1    |

2. The experimental design and optimization of the experiments were done using Statgraphics software.

2.4. Statistical Analysis and Mathematical Modeling.
2.4.1. Case 1: Presence of Anionic Surfactant (SDS). 2.4.1.1. Model Description and Optimization. A mathematical model was developed to relate the amount of adsorbed CH₄ in Marcellus shale to SDS concentration (C), salinity (S), and pressure (P). To optimize the model, only the parameters that have significant effects on the amount of adsorbed CH₄ were considered. Figure 2 shows all possible effects of pressure, salinity, and SDS concentration on the amount of adsorbed CH₄.

The bars that are extending beyond the black dotted reference line corresponds to effects that are statistically significant at a confidence level of 95%. The color of the bar indicates that the effect of the variable increases (gray) or decreases (blue) the amount of adsorbed CH₄. Optimizing the model requires neglecting all of the effects that are not significant at a confidence level of 95% including these quadratic and interaction effects, namely, PP, SS, CS, and CP. The optimized Pareto chart in Figure 3 highlights the effects of the factors that are significant in influencing the amount of adsorbed CH₄.

As shown in Figure 3, pressure (P) is the most significant variable that positively influences the amount of adsorbed CH₄. The effect of SDS concentration (C) and salinity (S) on the amount of adsorbed CH₄ is not significant at a confidence level of 95%. However, SDS concentration has a relatively large significant quadratic (CC) negative effect. Besides, the interaction between pressure and salinity seems to pose a significant negative effect on adsorbed CH₄. Despite its low main effects, salinity (S) was included in the model since it is involved in a significant interaction effect with pressure (SP). Similarly, SDS concentration (C) was included in the model despite its low effect since it has a significant quadratic effect (CC).

The final optimized mathematical model that describes the quantitative effects of pressure, SDS concentration, and salinity on the amount of adsorbed CH₄ is given in the following equation

\[ \eta_{\text{CH}_4} = -0.39332 + 2.97108C + 0.00294759S \\
+ 0.0173144P - 4.72204C^2 - 0.000251362SP \]

(1)

where \( \eta_{\text{CH}_4} \) is the amount of adsorbed CH₄ (mmol/g), C is the SDS concentration (wt %), S is the salinity (ppt), and P is the adsorption pressure (bar).

2.4.1.2. Main Variable Effects. Figure 4 highlights the main effects of the SDS concentration, salinity, and pressure on the amount of adsorbed CH₄ in Marcellus shale. At concentrations below the CMC, the amount of adsorbed CH₄ on Marcellus shale increases with the SDS concentration of the treating solution. Due to the affinity of shale to adhere to water, a proportion of the water from the treatment solution gets imbibed into the shale matrix. Once CH₄ is introduced into the treated shale sample during the adsorption process, an interface is created between CH₄ and the imbibed water within the shale matrix. As noted by many authors, increasing the surfactant concentration below the CMC reduces the surface tension at the liquid–gas interface. The highest reduction of surface tension by a surfactant is expected to occur at the CMC, beyond which increasing the surfactant

![Figure 1. Geometric representation of the Box–Behnken design.](image)

Table 3. Settings of Lower (−1), Central (0), and Upper (+1) Levels of Model Factors

| factor | unit | case 1     | case 2     |
|--------|------|------------|------------|
| P      | bar  | −1 25 50   | −1 25 50   |
| C      | wt % | 0.05 0.275 0.5 | 0.01 0.025 0.04 |
| S      | ppt  | 0.1 37.55 75 | 0.1 37.55 75 |
concentration causes no further decrease in surface tension.\textsuperscript{43−45} In this case, increasing the SDS (an anionic surfactant) concentration presumably caused the reduction of the surface tension in the liquid--CH\textsubscript{4} interface, which possibly allows a high amount of CH\textsubscript{4} to access the shale matrix and get adsorbed. The surface tension gets further reduced as the surfactant concentration increases, leading to even higher adsorbed CH\textsubscript{4} until a CMC of around 0.2 wt \% is reached. However, the amount of adsorbed gas fell after the CMC since negligible to no change in the surface tension at the liquid--gas interface occurs. Similar behavior was reported in previous studies, where the presence of an anionic surfactant at concentrations above the CMC was found to reduce the amount of adsorbed CH\textsubscript{4} in shale.\textsuperscript{8,10}

Figure 4 also shows that CH\textsubscript{4} adsorption in Marcellus shale decreases linearly upon increasing the salinity of the treatment solution. Treatment of the shale sample with water-based solution causes some water to be imbibed into the shale matrix. Once CH\textsubscript{4} is forced into the shale matrix during the adsorption experiment, it essentially interacts with the imbibed water. The decline in CH\textsubscript{4} adsorption in shale upon increasing the salinity is due to the salting-out effect, which occurs due to the interaction between the molecules of imbibed water and salts. The cations/anions that dissociate from dissolved salts surround most of the water molecules, and only a few water molecules can interact with CH\textsubscript{4}.\textsuperscript{46,47} Therefore, the saline water imbibed into the shale matrix during the treatment process is believed to lower CH\textsubscript{4} adsorption. Similar to the literature,\textsuperscript{48,49} CH\textsubscript{4} adsorption was found to linearly increase with pressure. Higher pressure exerts greater force in CH\textsubscript{4} molecules, hence forcing them to penetrate the shale matrix and get adsorbed.

### 2.4.1.3. Variable Interaction Effects

The effect of interaction between the independent factors on CH\textsubscript{4} adsorption in Marcellus shale was presented as a three-dimensional (3D) surface response with contour plots. These plots shown in Figures 5--7 are presented as a function of two varying factors, while the third factor was held constant at three different levels (lower level, center level, and upper level).

Figure 5 presents the amount of adsorbed CH\textsubscript{4} in Marcellus shale as a function of varying SDS concentrations (wt \%) and salinities (ppt) of the treatment solution, while adsorption
pressure is kept constant at the lower level (a), the central level (b), and the upper level (c).

Figure 5a–c shows that the maximum amount of adsorbed CH₄ in Marcellus shale samples increases with increasing the adsorption pressure. The highest amount of adsorbed CH₄ was about 1 mmol/g (Figure 5c) at 50 bar compared to just 0.3 mmol/g at 1 bar (Figure 5a). Such an observation is in line with previously published research studies,⁴⁸,⁴⁹ where CH₄ adsorption in shales was found to linearly increase with pressure. Higher pressure tends to force CH₄ molecules to penetrate the small pores existing in the shale matrix, which eventually leads to adsorption of the proportion of the intruded CH₄. At central and upper pressure levels, the maximum CH₄ adsorption was seen when the shale was treated with solutions of low salinities (0.1–20 ppt) and SDS concentration above the CMC (0.2 wt %). Such behavior is possibly attributed to the reduced surface tension at the CH₄–liquid interface and increased solubility of CH₄ due to the presence of SDS above its CMC at lower salinities.

Figure 6a–c displays the amount of adsorbed CH₄ into Marcellus shale as a function of varying pressures, salinities, and SDS concentrations at the (a) lower SDS level, (b) central SDS level, and (c) upper SDS level.

![Estimated response surface plots for CH₄ adsorption in Marcellus shale as a function of varying SDS concentrations and salinities and constant pressure at the (a) lower pressure level, (b) central pressure level, and (c) upper pressure.](image1)

![Estimated response surface plots for CH₄ adsorption in Marcellus shale as function of varying pressures, salinities, and SDS concentrations at the (a) lower SDS level, (b) central SDS level, and (c) upper SDS level.](image2)
According to the response and contour plots shown in Figure 6a−c, the highest amount of adsorbed CH₄ of nearly ∼1 mmol/g is obtained when the SDS concentration of the treatment solution was near or at a concentration of 0.275 wt % (Figure 6b). This concentration is somewhat close to its determined CMC, where the maximum reduction of surface tension at the liquid−gas interface is anticipated. Such low surface tension might allow a higher proportion of CH₄ molecules to penetrate through the liquid−gas interface and eventually get adsorbed in the shale matrix. However, the maximum amount of adsorbed CH₄ dropped to about 0.6 mmol/g (a 40% reduction) when the SDS concentration of the treating solution was below its CMC as shown in Figure 6a. The surface tension at the gas−liquid interface is expected to be relatively high when the surfactant concentration is below the CMC, which can reduce the amount of CH₄ penetrating into the shale matrix. At SDS concentrations above the CMC, the maximum adsorbed CH₄ was reduced to about 0.8 mmol/g (a 20% reduction), as shown in Figure 6c. Such a drop is possibly attributed to the formation of micelles at concentrations above the CMC, which might have occupied the sites available for CH₄. It is also interesting to note that the maximum adsorbed CH₄ in all cases Figure 6a−c occurred at a high pressure (∼50 bar) and a low salinity range (0.1−20 ppt).

As discussed earlier, the shale sample used is dominated by quartz (Table 1), which is associated with negative surface charge.³⁸ The interaction between the negatively charged head group of the anionic surfactant (SDS) and the shale surface is expected to cause repulsion between the surfactant molecules and the shale surface. Such behavior is assumed to reduce the amount of adsorbed surfactant solution into the shale matrix. Therefore, more sites will be available for CH₄ and that explains the relatively higher CH₄ adsorption in case 1 compared to case 2.

The response plots in Figure 7a−c present the amount of adsorbed CH₄ into Marcellus shale as a function of varying pressures and SDS concentrations, while salinity is kept constant at three levels, namely, the lower level (a), the central level (b), and the upper level (c). As seen in Figure 7a, the highest amount of adsorbed CH₄ (∼1 mmol/g) was found in the Marcellus shale samples that were treated with solutions of low salinity (0.1 ppt). The amount of adsorbed CH₄ was reduced to 0.6 and 0.3 mmol/g at salinities of 37.55 and 75 ppt, as shown in Figure 7b,c respectively. There is a noticeable decline in the amount of adsorbed CH₄ as the salinity increases. Such behavior could be explained as the solubility of CH₄ in the treatment fluid in a liquid decrease by the addition of a solute such as sodium chloride to the solution as reported by many authors.⁴⁶,⁴⁷,⁵⁰

### 2.4.1.4. Assessment of the Mathematical Model. Analysis of Variance (ANOVA): Table 4 shows the estimated effects of the selected factors and their associated P-values resulting from the analysis of variance of the proposed mathematical model described in eq 1. The table partitions the variability in adsorbed CH₄ into separate pieces for the effect of each factor, namely, pressure (P), SDS concentration (C), and salinity (S). Besides, it also highlights the significance of quadratic and
interaction effects of the variables. The statistical significance of each effect is also shown by comparing the mean square against an estimate of the experimental error. According to these results, pressure \((P)\) and salinity \((S)\) have \(P\)-values less than 0.05, indicating that they significantly influence the amount of adsorbed \(\text{CH}_4\) at a confidence level of 95.0\%. Similarly, the quadratic effect of \(\text{CC} \ (P\text{-value} = 0.0137)\) and the interaction effect of \(SP \ (P\text{-value} = 0.0178)\) are significant parameters in the mathematical model.

**Confidence of the Model 1**: To assess the robustness of the mathematical model described in eq \(4\), the measured adsorbed \(\text{CH}_4\) in Marcellus shale was compared to the amount of adsorbed \(\text{CH}_4\) predicted by the model. Figure 8 shows the goodness of the model in eq \(1\), given by the \(R^2\) of 0.82, which means that the proposed model can explain 82\% of the variability in adsorbed \(\text{CH}_4\) (mmol/g). The model was also tested for autocorrelation in the residuals using Durbin–Watson (DW) statistic tests. The test resulted in a DW statistic of 2.48, indicating no autocorrelation in the residuals.

**Error Analysis**: Residual or error analysis was performed to further assess the quality of the mathematical model described in eq \(1\). The error analysis aims to inspect the primary statistical assumptions about residuals such as constant variance, independence of variables, and normality of the distribution. For a good and representative regression model, the residuals would have to be randomly distributed around zero. Figure 8 shows a plot residual vs run number for the mathematical model for case 1. The plot facilitates examining the drift of the variance during the experimental process. As Figure 9 suggests, the residuals are randomly distributed around zero, and there exists no trend on the plot, indicating that the model is good.

### 2.5. Case 2: Presence of a Cationic Surfactant

#### 2.5.1. Model Description

A mathematical model was developed to relate the amount of adsorbed \(\text{CH}_4\) in Marcellus shale to the CTAB concentration \((C)\), salinity \((S)\), and pressure \((P)\). The model was first optimized to include only the parameters that have significant effects on the amount of adsorbed \(\text{CH}_4\). Figure 10 shows all possible effects of pressure, salinity, and CTAB concentration on the amount of adsorbed \(\text{CH}_4\). The bars that are extending beyond the black dotted reference line corresponds to effects that are statistically significant at a confidence level of 95\%. The color of the bar indicates that the effect of the variable increases (gray) or decreases (blue) the amount of adsorbed \(\text{CH}_4\). As shown in Figure 10, pressure \((P)\) is the most significant variable that positively influences the amount of adsorbed \(\text{CH}_4\) followed by CTAB concentration \((C)\). Salinity \((S)\) does not appear to influence the amount of adsorbed \(\text{CH}_4\) significantly. However, the interaction between CTAB concentration and salinity \((CS)\) seems to pose a significant positive effect on adsorbed \(\text{CH}_4\). In addition, pressure has a relatively large significant quadratic \((PP)\) positive effect, while the quadratic effect of the CTAB concentration \((CC)\) is quite important in effecting the model. Other quadratic effects and interaction effects such as \(SS, SP,\) and \(PC\) do not seem to affect the amount of adsorbed \(\text{CH}_4\) significantly.

The optimized Pareto chart in Figure 11 highlights the important effects of the factors that are significant in influencing the amount of adsorbed \(\text{CH}_4\). All other insignificant effects were taken into consideration when formulating the model.

The developed mathematical model that describes the quantitative effects of pressure, CTAB concentration, and salinity on the amount of adsorbed \(\text{CH}_4\) is shown in the following equation

\[
\eta \text{CH}_4 = 0.0653584 + 0.000841003P - 0.00125025S
- 6.72768C + 0.0005797912P^2 + 0.0644799CS
+ 121.017C^2
\]

where \(\eta \text{CH}_4\) is the amount of adsorbed \(\text{CH}_4\) (mmol/g), \(C\) is the CTAB concentration (wt \%), \(S\) is the salinity (ppt), and \(P\) is the adsorption pressure (bar).

#### 2.5.2. Main Variable Effects

Figure 12 presents the main effects of pressure, salinity, and the CTAB concentration on the amount of adsorbed \(\text{CH}_4\) in Marcellus shale, which is described in eq \(5\). Similar to case 1, the amount of adsorbed \(\text{CH}_4\) increases with pressure. Higher pressure forces \(\text{CH}_4\) molecules to go through the shale matrix, and such an interaction provides a higher chance for \(\text{CH}_4\) adsorption to occur. Surprisingly, the amount of adsorbed \(\text{CH}_4\) in Marcellus shale was found to slightly increase with salinity. However, the possible reasons for such behavior are not clearly understood.

An insignificant decrease in the amount of adsorbed \(\text{CH}_4\) was noted as the CTAB concentration increases until reaching the CMC \((\sim 0.029 \text{ wt }\% )\), above which the amount of adsorbed \(\text{CH}_4\) increased with increasing CTAB concentration. Increasing the CTAB concentration causes the reduction of the surface tension in the liquid–gas interface, which possibly allows a high amount of \(\text{CH}_4\) to get adsorbed into the shale.
matrix. The surface tension gets further reduced as the CMC of CTAB concentration is achieved at around 0.029 wt %. The contrary behavior of SDS and CTAB in CH$_4$ adsorption (Figure 4 vs Figure 12) could potentially be due to the differences in the charges between SDS and CTAB. SDS is an anionic surfactant that is negatively charged, while CTAB is a cationic surfactant that is positively charged.

2.5.3. Variable Interaction Effects. Similar to case 1, the effect of interaction between independent factors on CH$_4$ adsorption in Marcellus shale was further analyzed and presented as a 3D surface response with contour plots. These plots shown in Figures 13−15 were presented as a function of two factors, while the third factor was fixed at three different levels (lower level, center level, and upper level).

Figure 13 shows the estimated surface of the amount of adsorbed CH$_4$ into Marcellus shale as a function of varying CTAB concentrations (wt %) and salinities (ppt), while the pressure is kept constant at the lower level (a), the central level (b), and the upper level (c). The maximum amount of adsorbed CH$_4$ (∼0.3 mmol/g) is achieved at an upper pressure level (50 bar) as shown in Figure 13c. At a central pressure level of 25 bar as shown in Figure 13b, the maximum amount of adsorbed CH$_4$ was nearly half of that achieved at 50 bar (0.15 mmol/g).

Such an observation is in line with previously published research studies, where CH$_4$ adsorption in shale was reported to linearly increase with pressure. Higher pressure tends to force CH$_4$ molecules to penetrate the small pores existing in the shale matrix, which eventually leads to the adsorption of a proportion of the intruded CH$_4$. It is also important to note that the maximum amount of adsorbed CH$_4$ in the three cases shown in Figure 13 was found on shale samples treated with solutions of high salinities and CTAB concentration above the CMC.

The 3D response plots in Figure 14a−c show the amount of adsorbed CH$_4$ into Marcellus shale in mmol/g as a function of varying salinities (ppt) and pressures, while the CTAB concentration (wt %) is kept constant at three different levels, namely, (a) the lower level/below the CMC, (b) the central level/at the CMC, and (c) the upper level/above the CMC.

The highest amount of adsorbed CH$_4$ of nearly ∼0.3 mmol/g is obtained at a CTAB concentration of 0.04 wt % at high pressure, as shown in Figure 14c. Such a concentration is well above the CMC of the CTAB surfactant. For any given surfactant, the maximum reduction of surface tension at the liquid−gas interface is anticipated at concentrations at and above the CMC. The low surface tension induced by CTAB existing at a concentration above its CMC had possibly allowed more CH$_4$ molecules to penetrate through the liquid−
gas interface, where they eventually get adsorbed in the shale matrix.

Figure 14a shows that the maximum amount of adsorbed CH$_4$ in Marcellus shale at CTAB concentrations below its CMC (e.g., 0.025 wt %) was found to be 0.2 mmol/g. This amount was achieved at the high-pressure region and at lower salinity, and it is relatively lower than that achieved at CTAB concentrations above its CMC. The decline in the amount of adsorbed CH$_4$ in shale is possibly attributed to the relatively higher surface tension at liquid–gas associated with the existence of CTAB at a concentration below its CMC. Such higher surface tension presumably reduces the amount of CH$_4$ penetrating the shale matrix.

The 3D response plots in Figure 15a–15c present the amount of adsorbed CH$_4$ in Marcellus shale samples that were treated with aqueous solutions containing NaCl and CTAB surfactant. The results are shown as a function of pressure and CTAB concentration while salinity is kept constant at three distinct levels, namely, the lower salinity level (a), the central salinity level (b), and the upper salinity level (c).

The possible interaction between the head group of the cationic surfactant (CTAB), which is positively charged, and the shale surface is expected to cause attraction between the
surfactant molecules and the shale surface. Such behavior is assumed to increase the amount of adsorbed surfactant solution into the shale matrix. Therefore, few sites will be available for CH₄, and that explains the lower CH₄ adsorption in case 2 compared to case 1.

As suggested by Figure 15a−15c, increasing the salinity of the treatment solution is generally associated with an increase in the amount of adsorbed CH₄ in the shale sample. As seen in Figure 15c, the highest amount of adsorbed CH₄ (∼0.27 mmol/g) was achieved when the aqueous solution used from shale treatment was at a higher salinity level (75 ppt) provided that the CTAB concentration was above the CMC. The pressure required to attain the maximum amount of CH₄ adsorption was nearly 50 bar. At a lower salinity level or freshwater (0.1 ppt) as in Figure 15a, the maximum amount of adsorbed CH₄ in the shale sample was reduced to ∼0.2 mmol/g. At an intermediate salinity level (37.55 ppt) as shown in Figure 15b, the amount of adsorbed CH₄ in Marcellus shale increased to about 0.22 mmol/g as long as the CTAB concentration was well above the CMC.

Apparently, the coexistence of salt and CTAB in the aqueous solution used for shale sample treatment has a significant synergistic effect on CH₄ adsorption. Figure 16 visualizes the implication of NaCl−CTAB interaction on CH₄ adsorption in Marcellus shale. At CTAB concentrations below its CMC (e.g., 0.1 wt %), increasing the salinity of the treatment solution tends to reduce the amount of adsorbed CH₄. However, increasing the salinity was found to increase the amount of adsorbed CH₄ if CTAB was used at concentrations above its CMC (e.g., 0.04 wt %). Higher salinity has presumably forced CTAB to accumulate at the shale−liquid and/or liquid−CH₄ interfaces, which in turn enhanced the reduction in surface tension. Such a reduction of surface tension is expected to allow CH₄ to penetrate the shale matrix, hence increasing the possibility of CH₄ adsorption. The findings correlate with some earlier studies, where the combined effect of CTAB and NaCl was reported to lower the surface tension and surface energy of a hydrocarbon phase in the presence of surfactant solution.33,53

2.5.4. Assessment of the Mathematical Model. Analysis of Variance (ANOVA): Table 5 shows the estimated effects of the factors and their associated P-values, resulting from the analysis of variance of the proposed mathematical model described in eq 2. The table partitions the variability in adsorbed CH₄ into separate pieces for the effect of each factor, namely, pressure (P), CTAB concentration (C), and salinity.

![Estimated response surface at salinity = 0.1 ppt](image1)

![Estimated response surface at salinity = 37.55 ppt](image2)

![Estimated response surface at salinity = 75 ppt](image3)

Figure 15. Response surface plots for CH₄ adsorption in Marcellus shale as a function of varying CTAB concentrations and pressures and constant salinity at the (a) lower salinity level, (b) central salinity level, and (c) upper salinity level.

![Synergistic effect of NaCl and CTAB concentration on CH₄ adsorption](image4)

Figure 16. Synergistic effect of NaCl and CTAB concentration on CH₄ adsorption.

| source | sum of squares | mean square | P-value |
|--------|---------------|-------------|---------|
| P      | 0.00699217    | 0.00699217  | 0.0000  |
| S      | 0.00146824    | 0.00146824  | 0.1466  |
| C      | 0.00547724    | 0.00547724  | 0.0146  |
| PP     | 0.00487596    | 0.00487596  | 0.0190  |
| SC     | 0.00524801    | 0.00524801  | 0.0161  |
| CC     | 0.00275381    | 0.00275381  | 0.0588  |
| total error | 0.00454519 | 0.000568149 |         |
| total (corr.) | 0.0938031 |            |         |

Table 5. ANOVA Results for the Case 2 Model
Besides, it also highlights the significance of quadratic (PP, CC, and SS) and interaction effects (SC) of the variables. The statistical significance of each effect is also shown by comparing the mean square against an estimate of the experimental error. According to these results, four factors have P-values less than 0.05 (P, C, PP, and SC), indicating that they are significantly different from zero at a confidence level of 95.0%.

Confidence of Model 2: The measured adsorbed CH₄ in Marcellus shale was compared to the amount of adsorbed CH₄ predicted by the model (eq 2). Figure 17 shows the goodness of the model in eq 2, given by the $R^2$ of 0.94, which means that the proposed model can explain 94% of the variability in adsorbed CH₄ (mmol/g). The model was also tested for autocorrelation in the residual using Durbin–Watson (DW) statistic tests. The test resulted in a DW statistic of 2.39, indicating no autocorrelation in the residuals.

Error Analysis: Error analysis was performed to further assess the robustness of the mathematical model presented in eq 2. Similar to case 1, the error analysis aims at inspecting the primary statistical assumptions about residuals such as constant variance, independent of variables and normality of the distribution. The residuals should be randomly distributed around zero in good regression models. Figure 18 shows a plot of residual vs run number, showing that residuals appear to be randomly distributed around zero, and there exists no trend on the plot. Therefore, it is an indication that the mathematical model is good enough to describe the experimental data.

3. CONCLUSIONS
The influence of surfactants, salinity, and pressure on CH₄ adsorption in Marcellus shale samples was evaluated through a series of DOE-based experiments. As a result of this study, the following general and specific observations and conclusions may be drawn:

- In general, treatment of shale with surfactant solution showed an enhancement in the amount of adsorbed CH₄ at certain ranges of surfactant concentration and salinity. However, opposite behavior is observed at some other ranges of the said parameters, for instance, above and below the CMC of the surfactant.
- The maximum amount of adsorbed CH₄ in Marcellus shale samples increases with increasing adsorption pressure.
- In the presence of the SDS surfactant, the highest amount of adsorbed CH₄ was about 1 mmol/g, which was achieved at 50 bar adsorption pressure, salinities ranging from 0.1 to 20 ppt, and an SDS concentration close to its CMC (0.2 wt %).
- However, the maximum amount of adsorbed CH₄ dropped to about 0.6 mmol/g (a 40% reduction) when the SDS concentration of the treating solution was below its CMC.
- At an SDS concentration above the CMC, 20% reduction was noted on the maximum adsorbed CH₄.
- In the presence of the CTAB surfactant, the maximum amount of adsorbed CH₄ is nearly 0.3 mmol/g, which was achieved at the upper pressure level (50 bar), high salinities, and CTAB concentration above the CMC (>0.029 wt %).
- At a CTAB concentration below the CMC, 20% reduction in adsorbed CH₄ was noted (adsorbed CH₄ reached ∼0.2 mmol/g below the CMC).

4. RECOMMENDATIONS
- More research studies should be devoted to deciphering the reasons behind the changes in CH₄ adsorption behaviors due to treatment with SDS and CTAB surfactant solutions at varying temperatures.
- It is recommended to assess the capability of other popular surfactants in altering the CH₄ adsorption characteristics in shale.

5. EXPERIMENTAL SECTION
5.1. Materials. 5.1.1. Surfactants. SDS, an anionic surfactant, and CTAB, a cationic surfactant, was utilized in this research. The surfactants are commonly used in a wide range of applications in enhanced oil recovery (EOR) processes. SDS was purchased in powder form from Sigma-Aldrich, and CTAB was procured from Acros Organics in powder form. Figure 19 displays the molecular structures of SDS and CTAB detailing their hydrophobic carbon chain tail and hydrophilic (lipophilic) polar groups.
within Marcellus formation, which belongs to the Late Cretaceous. SDS and CTAB promote gas hydrates such as CH$_4$ and hydrocarbons, respectively. A higher HLB value indicates a greater hydrophilicity behavior, while smaller HLB will result in a surfactant with more lipophilic groups. Trace elements present in the shale sample were quantified by fluorescence (XRF) analysis.

### Table 6. Information’s of the Used Surfactants

| surfactant | type    | purity (%) | MW (g/mol) | HLB | CAS$^b$ | provenance |
|------------|---------|------------|------------|-----|--------|------------|
| SDS        | anionic | 99.0       | 288.4      | 40$^a$ | 151-21-3 | Sigma-Aldrich |
| CTAB       | cationic| 99         | 364.4      | 15.8$^a$ | 57-09-0 | Acros Organics |

$^a$From ref 54. $^b$CAS stands for Chemical Abstracts Service.

### Table 7. Summary of Equations Used for Calculating the Amount of Adsorbed CH$_4$ in Shale Samples

| purpose | equation | no. |
|---------|----------|-----|
| to determine the number of CH$_4$ moles ($n_{\text{CH}_4}$) flowed from the reference cell into the adsorption cell; the equation is used for each adsorption cell | $n_{\text{CH}_4} = \frac{V_f (P_f - P_i) Z_f - Z_t}{R T}$ | (1) |
| to determine the equilibrium pressure ($P_{\text{CH}_4}$) | $P_{\text{CH}_4} = P_t - P_r$ | (2) |
| to determine the amount of CH$_4$ present in the gas phase within the adsorption cell | $n_{\text{CH}_4(g)} = \frac{V_f P_{\text{CH}_4}}{Z_{\text{CH}_4} R T}$ | (3) |
| to determine the number of moles of CH$_4$ absorbed ($n_{\text{CH}_4(abs)}$) in the shale sample | $n_{\text{CH}_4(abs)} = n_{\text{CH}_4} - n_{\text{CH}_4(g)}$ | (4) |

$^a$ $V_t$ is the volume of the reference cell, $R$ is the gas constant, $T$ is the temperature in the reference cell, $P_r$ and $P_i$ are the initial and final pressures in the reference cell, respectively, and $Z$ is the compressibility factor. $P_{\text{CH}_4}$ is the equilibrium pressure, $P_t$ is the total pressure in the adsorption cell, and $P_r$ is the vapor pressure of the solution imbibed into the shale sample during the treatment process, which was assumed to be negligible due to the ultralow volume of imbibed solution into the shale matrix. $n_{\text{CH}_4(g)}$ is the amount of CH$_4$ present in the gas phase. $V_f$ is the gas phase volume, $Z_{\text{CH}_4}$ is the compressibility of $P_{\text{CH}_4}$, and $T$ is the temperature in the adsorption cell.

Shale Samples. The shale sample was collected during a field work from the Chattanooga member of Marcellus shale formation. Chattanooga is a gas shale member within Marcellus formation, which belongs to the Late Devonian age. The shale sample is black in color and has some interbedding layers of gray color. A stock of powdered shale was prepared by crushing the shale sample into fine powders and was then used in the experiments. The major, minor, and trace elements present in the shale sample were quantified by performing X-ray fluorescence (XRF) analysis.

Methods. 5.2.1. Surfactant CMC Measurement. CMC is defined as the surfactant concentration above which micelles starts to form. A Cary 60 UV−vis spectrophotometer (Agilent Technologies, Australia) was utilized for CMC determination of the two surfactants. According to the literature, this is a well-established method for the determination of the surfactant CMC. The light absorbance of the SDS solutions of different concentrations was measured at a wavelength of 500 nm. A similar measurement was carried out for CTAB solutions at a wavelength of 320 nm. At a given set of experimental conditions, light absorbance varies linearly with the surfactant concentration. However, such linearity is disturbed by the formation of micelles, which is the principal basis for obtaining the CMC by a UV−vis spectrophotometer. The measured absorbances were plotted vs surfactant concentration, and the CMC for each surfactant was taken from the plot taken as the surfactant concentration where a sudden change of slope occurs. In the oil and gas industry, the determination of surfactant CMC is essential prior to using them for any application. At concentrations below the CMC, interfacial tension (IFT) and surface tension between liquid−liquid and liquid−solid interfaces are not reduced effectively. Therefore, surfactants are used at concentrations higher than the CMC when the lowest IFT or surface tension is desired.

5.2.2. Solution Preparation and Shale Treatment. Different surfactant solutions at different concentrations and salinities were prepared. The continuous phase for each solution was water at a certain salinity, while the dispersed phase was a surfactant. The salinity was varied using NaCl across a wide range from 0.1 to 75 ppt, and electrical conductivity was ranging from 800 to 58 000 μS/CM. These solutions cover salinities of freshwater, brackish water, seawater, and brine. For each surfactant, three concentrations were used, namely, (a) below the CMC, (b) at the CMC, and (c) above the CMC. The surfactant solutions of different concentrations were prepared by mixing a predetermined mass of surfactant powder into brine and then mixed using a magnetic stirrer. Shale treatment was achieved by mixing 5 g of powdered shale with 5 mL of surfactant solution inside a closed tube. The mixing process was achieved using a magnetic stirrer for 10 min. This was followed by an aging step where the shale sample is immersed for 2 h in a closed tube containing the surfactant solution while agitating in temperature-controlling shaking apparatus at 120 rpm and 30 °C. The aging time of 2 h was used for all cases to avoid any discrepancies.

5.2.3. CH$_4$ Adsorption. CH$_4$ adsorption measurement was performed utilizing a pressure cell that was manufactured by DIXSON, Malaysia (SN-0115). The reader should refer to the published article in ref 65, which provides details about the equipment and the procedures it follows to measure the amount of adsorbed gas. In this study, similar procedures were adopted to determine the amount of adsorbed gas in Marcellus shale. The experiments were carried out by allowing CH$_4$ to react with Marcellus shale samples in the pressure equilibrium cells. After purging the 5000 mL premixed tank (reference cell) and each of 50 mL adsorption cells (cells 1−3) with nitrogen (N$_2$), 5 g of crushed shale sample was loaded into each of the three adsorption cells. CH$_4$ gas was first allowed to transfer into the 5000 mL reference cell (premixed tank) to achieve the desired pressure. When the required pressure is achieved, CH$_4$...
was then allowed to flow from the reference cell into the adsorption cells (cells 1–3) batch by batch. It is important to mention that baseline measurements of CH₄ adsorption were performed on a dry shale sample, which was then followed by other sets of CH₄ adsorption tests on the treated shale samples. One set of measurements was performed on shale samples treated with anionic surfactant solution (SDS), while the other set was carried out on shale samples treated with a cationic surfactant solution (CTAB).

The equations (eqs 3–5) that are summarized in Table 7 for calculating the amount of adsorbed CH₄ were developed by Mohamed Mohsin et al., who used the same equipment for other sets of CH₄ adsorption tests on the treated shale samples.

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**Notes**

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