Carbonate Stimulation Using Chelating Agents: Improving the Treatment Performance by Optimizing the Fluid Properties

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ABSTRACT: Chelating agents’ solutions were introduced as effective alternatives to strong acids to be used in acid-sensitive situations such as high temperature and salinity conditions. However, limited studies have been conducted to examine the optimum conditions for improving the chelating agent performance. In this study, a comprehensive study of solubility and physical properties of different chelating agents’ fluids that are commonly used in the oil upstream applications was performed under different conditions. The optimum concentration ranges at which chelating agents are soluble and effective to provide the best acidizing efficiency are determined. Also, more than 340 data sets were used to develop new empirical models that can help in estimating the chelating agents’ properties at wide ranges of concentrations and treatment temperatures. In this work, different experimental measurements were conducted using a pressure of 2000 psi (13.7 MPa) and a temperature of 120 °C (393.15 K). The conducted experiments are density and viscosity measurements, solubility experiments, interfacial tension measurements, computed tomography scan, and coreflooding tests. The used chelating agents are diethylenetriaminepentaacetic acid (DTPA), hydroxyethylenediaminetriacetic acid (HEDTA), and ethylenediaminetetraacetic acid (EDTA). Results revealed that HEDTA and DTPA chelating agents have good solubility at different pH and concentration ranges. However, EDTA showed a limited solubility performance, especially at a concentration greater than 15 wt %. Moreover, the developed correlations provided fast and reliable estimations for the chelating agent density and viscosity, and estimation errors of around 1% were achieved. Also, treating the tight carbonate rocks with the optimized chelating agent solutions showed effective wormholes with a minimum acid volume. Finally, a good match between the actual and predicted pressure drops is achieved, confirming the high reliability of the developed models. Overall, this work can help in designing the stimulation treatment by suggesting the optimum ranges for fluid concentration and solution pH for wide ranges of temperature. Also, the newly developed correlations can be used to provide quick and reliable estimations for the pressure drop and the chelating agent properties at reservoir conditions.

1. INTRODUCTION

Production and injection wells are usually stimulated every 3 to 5 years, depending on the reservoir and well conditions, to restore or improve the well productivity/injectivity.1−4 The formation damage can be induced during drilling, completion, and most likely during production or injection operations.5−8 The invaded drilling mud or completion fluids can induce severe formation damage due to the reaction between these fluids and the reservoir system.4,7,9−11 Hence, a low permeability zone will be created around the wellbore, which will reduce oil or gas production significantly. Carbonate rocks are mostly affected by formation damages compared to sandstone formations due to their strong reactivity with any fluid that contacts the rock surface. Therefore, frequent stimulation operations are conducted to remove the damages and improve the formation productivity.4,7−9

Usually strong acids such as hydrochloric acid (HCl) and hydrofluoric acid (HF) are used to stimulate the carbonate reservoirs.12−14 HCl and HF have very strong reactivity, which can lead to high acidizing performance by creating wormholes in the wellbore-neighboring region.14 However, HCl and HF are corrosive fluids; hence, corrosion inhibitors are injected during the carbonate stimulation treatment.12,15 Although corrosion inhibitors are used, tubular corrosion cannot be avoided with such strong acids. Also, conventional acids such as hydrochloric and organic acids can only be used with freshwater because they are incompatible with seawater.2,16 Given this, the freshwater transportation will increase the...
treatment cost, especially for offshore operations where the acidizing treatment cost could be increased by more than $100,000. Therefore, applying simulation treatment using freshwater would be very costly, especially for offshore operations. Consequently, new formulations of acids systems were introduced to slow down the corrosion process and minimize the use of freshwater. These new formulations can be used to stimulate shallow formations as well as deep formations under high-temperature conditions, where most of the strong acids induce severe corrosion problems due to the high reaction rate.

Strong acid-associated problems led to the investigation and use of weak organic acids as standalone stimulation fluids. This investigation concluded that acetic, citric, formic, and lactic acids can be efficiently used as alternatives to strong acids for situations where they are not recommended to be used such as shallow wells and high-temperature wells. However, the laboratory studies on some of these organic acids showed that precipitation of calcium salts made a noticeable impact on the corrosion properties inside the carbonate rocks, and this impact is clear at high temperatures. Also, organic acids have limited solubility in water and cannot be used at high concentrations to avoid precipitations and damage related to these acids.

It is well-known that chemical solubility is one of the main parameters that control the applicability of any acid system. Using an acid with low solubility for stimulating sandstone or carbonate reservoirs can result in negative impacts, and the reservoir productivity will be reduced due to the incompatibility and precipitation issues. Thus, considerable attention should be paid to selecting the proper acid system based on particular reservoir composition and conditions.

In the oil industry, chelating agents were first used as formation damage removal to eliminate the damages created by drilling and completion fluids. They were found to be efficient in removing most of the drilling and completion damages. Also, these chemicals can be injected to remove different scales types from the production system. In 1996, Freed and Fogler reported the first use of chelating agent solutions as standalone fluids for stimulation treatments. The rate of calcite dissolution by chelating agents was investigated for different pH values and chelating types. The performance of ethylenediaminetetraacetic (EDTA), diethylenetriaminepentaacetic (DTPA), and cyclohexanediiminetetraacetic acids for stimulating carbonate rocks was extensively studied. Several studies proved that chelating agents can be used as an alternative to HCl acid and weak organic acids for acidizing different formations. Other chelating agents such as hydroxyethylenediaminetriacetic acid (HEDTA) and L-glutamic acid were also studied and proved their effectiveness in stimulating carbonate rocks positively with less corrosion to the well tubular and less damage to the rock.

Chelating agents can be used to stimulate the reservoir formations without weakening the rocks or inducing solid production after the stimulation treatment. Chelating agents are recently involved as standalone simulation fluids; however, no comprehensive work has been conducted to determine the optimum fluid behavior that will lead to optimizing the treatment efficiency. Parameters such as fluid compatibility, density, and viscosity are not well-examined in the literature. The performance of carbonate acidizing can be improved by selecting the optimum fluid properties, which will result in reducing the injection pressure, acid volume, and treatment duration. The novelty of this work is proposing new models that can help significantly in improving the design of acidizing treatment by providing a quick and reliable estimation for the treatment efficiency based on the operational parameters. In this work, three effective chelating agents (which are commonly used in the industry) were studied at a wide range of pH, chemical concentration, and temperature values. The optimum fluid characteristics for EDTA, DTPA, and HEDTA chelating agents were estimated. Also, the interfacial tension (IFT) between chelating agents and crude oil was measured. Finally, new correlations were developed, utilizing more than 350 laboratory measurements, to estimate the fluid properties of chelating agents as functions of temperature and concentration.

2. MATERIALS AND EXPERIMENTAL WORK

2.1. Materials. In this work, three types of chelating agents were used: Na₂EDTA, Na₅DTPA, and Na₃HEDTA. Chelating agents were purchased from Scharlau company, and the used chemicals have a purity of more than 99%. The molecular weights are 372.24, 503.26, and 344.20 g/mol for Na₂EDTA, Na₅DTPA, and Na₃HEDTA, respectively. All chemicals were received in powder forms, and then, the solutions were prepared using deionized (DI) water and seawater brine. The used chelating agents have original concentrations of 37–41 wt % and pH values of 7.5–12.0. These chelating agents were selected because of their effective stimulation performance compared to that of other chelating agents.

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In addition, DI water was used as a reference fluid to minimize the complexity associated with the ions present in seawater. The solution pH was adjusted by using a few droplets of hydrochloric (HCl) and sodium hydroxide (NaOH), without considerable changes in the fluid properties. Moreover, 3 wt % KCl brine was utilized to saturate the carbonate samples and to measure the absolute rock permeability, by injecting the KCl brine at various rates and recording the differential pressure across the rock sample.

In addition, tight carbonate rocks from the Indiana limestone formation were used, and the samples were purchased from Kocurek Industries INC. The rock samples were characterized to estimate their petrophysical properties. The used samples have an average permeability of 0.5–7 mD and a porosity of 10.2%. The rock samples were treated by the optimized chelating agent, and the absolute permeability was determined before and after the chemical injection. The primary objective is to create a continuous wormhole along the treated rock, leading to huge improvements in the rock permeability.

2.2. Experimental Work. The fluid properties of chelating agents’ solutions were evaluated at different chemical concentrations, temperatures, and calcium concentrations. Liquid hydrometers purchased from Fischer company and a capillary viscometer manufactured by Koehler company were used to measure the fluid densities and viscosities, respectively. The measurements were conducted following the common standard procedures to ensure a high level of reliability. The chelating agents were prepared at the required concentration;
then, the fluid properties were evaluated at different temperatures ranging from 72 to 212 °F (295.3 to 373.15 K). After that, the impact of calcium ion concentration on the fluid properties was assessed by preparing the chelating agents at different concentrations of calcium ions and measuring the density and viscosity at various temperatures. Finally, results from 350 fluid experiments were collected and plotted. The multi-fitting technique was used to establish relationships between the fluid properties and the studied parameters.

In addition, the IFT between different concentrations of chelating agents and crude oils of different American Petroleum Institute (API) gravities was assessed using an optical tensiometer. Three crudes that have API gravities of 31.18, 35.6, and 40° API were used, and these API gravities were used to represent wide ranges of crude oils; heavy, medium, and light oils. The IFT measurements were conducted by keeping the oil droplet in tension using a chelating agent until the system stabilization was achieved. Moreover, a compatibility study and coreflooding measurements were performed to determine the performance of chelating agents in stimulating carbonate rocks. The carbonate stimulation treatments were carried out using high pressure and high temperature situations. The optimized chelating agent was injected into tight carbonate rocks to induce wormholes and improve the absolute permeability. Two core samples from Indiana Limestone rocks were selected for acid stimulation. The rock dimensions, porosities, permeability, chelating agent type and concentration, and injection rate are provided in Table 1. The core samples were fully saturated using the KCl brine (3 wt %) under high pressure conditions, a core holder, fluid accumulators, injection pumps, and pressure gauges was used in this work. The acid injection experiments were conducted using a temperature of 250 °F (394.26 K), a confining pressure of 2000 psi (13.7 MPa), and a backpressure of 1000 psi (6.9 MPa). The chelating agent was injected at 0.5 cc/min for the first core sample and 1.0 cm³/min for the second core sample. The injection of the chelating agent’s solutions was continued until continuous wormholes were created across the length of each core sample. Computed tomography (CT) scan was conducted using the Toshiba Alexion TSK-032A equipment that can provide a resolution of 1 mm. The CT scan was performed for the carbonate samples after the treatment to emphasize the generation of wormholes. During the flooding tests, the pore pressure along the carbonate samples was monitored. The pressure profiles were compared with the predicted profiles based on the developed equations, where a good agreement was observed between the actual pressure drop and the predicted pressure drop.

## Table 1. Rock Properties, Chelating Agent Types, and Injection Rates Used for the Acidizing Experiments

| parameter                  | sample A | sample B |
|----------------------------|----------|----------|
| length, in.                | 5.85     | 5.93     |
| diameter, in.              | 1.50     | 1.50     |
| porosity, fraction         | 0.10     | 0.10     |
| permeability, mD           | 0.94     | 0.62     |
| chelating agent’s type     | HEDTA    | HEDTA    |
| chelating agent’s concentration, % | 20      | 15       |
| injection rate, cm³/min    | 0.5      | 1.0      |

# 3. RESULTS AND DISCUSSION

## 3.1. Solubility of Chelating Agents

### 3.1.1. Preparation of Chemical Solutions Using DI Water

DI water was used as a reference fluid to study the fluid properties of chelating agents at different concentrations without introducing the complexity associated with seawater ions. After understanding the fluid behavior at different conditions, the acid solutions were prepared using seawater, which will minimize the cost and represent the actual field applications. Various solutions were prepared with a wide range of chemical concentrations using DI water. Figure 1 illustrates the solubility profiles for chelating agents at various concentrations and solution pH values. The fluid pH showed a significant impact on the Na₂EDTA solubility, particularly at concentrations of more than 20 wt %. For example, for 20 wt % Na₂EDTA, the chelating agent solution will be clear without precipitation only for a pH higher than 6.5. Using EDTA at a concentration more than 20 wt % required a minimum solution pH of 7 to ensure no precipitation. Usually, EDTA is used with a concentration between 15 and 20 wt % for stimulation treatments, and then, the solution pH is recommended to be more than 6.5 to avoid any formation plugging due to the solid precipitation. On the other hand, the solution pH showed little impact on the chelate solubility for Na₅DTPA and Na₅HEDTA, and clear and fully soluble chelates were obtained for all pH values higher than 2; even for highly concentrated solutions (up to 40 wt %) no precipitations were observed for a pH higher than 2. Ultimately, it is not recommended to use Na₅EDTA chelating agents as the stimulation fluid at a pH lower than 6.5. The concentration of stimulation fluids was recommended by many studies to be 15–20 wt %, and for Na₅EDTA to have such a concentration, the pH should be maintained to be more than 6.5. Using low pH values (less than 6.5) can result in solid precipitation, which will impact the efficiency of the fluid during the acidizing process and will cause severe formation damage. Na₅DTPA and Na₅HEDTA chelating agents can be used safely at any concentration at pH values as low as 2 if the dilutions are performed using DI water.

#### 3.1.2. Preparation of Chemical Solutions Using Seawater

Generally, the chelating agents are fully soluble at high pH, so in this work, our consideration is to determine the minimum pH at which the chelating agent solutions can be prepared without any precipitation. The chelating agents’ solutions were prepared at different pH values and concentrations; then, the solutions were investigated to observe any precipitations; and hence, the solubility ranges were determined. The solubility profiles for chelating agents at various pH values and concentrations are shown in Figure 2. All solutions were prepared using seawater. Similar to the solutions prepared using DI, the pH does not affect the chelate solubility for Na₅HEDTA and Na₅DTPA. These chelating agents were fully soluble in the seawater even at a low pH of around 2. However, the solubility of Na₂EDTA powder was considerably affected by the solution pH. It was not possible to have a soluble solution from Na₂EDTA when the pH is below 5.4. For example, preparing EDTA solutions of 20 wt % or higher showed considerable precipitations at low pH values of less than 7. Therefore, it is recommended to use EDTA solution at pH more than 7, when the solution concentration is 20 wt % or higher. Overall, it is concluded that all chelating agents are fully soluble at pH more than 7, and no participation was observed for all concentrations using seawater or DI water. Also, it is...
found out that only EDTA is not soluble at a pH lower than 3.0 when the solutions are prepared using DI water. However, preparing the EDTA solutions using seawater requires increasing the pH to 5.4 or more to avoid solid precipitations. Ultimately, using seawater for preparing the EDTA solutions would reduce the chemical solubility especially at high concentrations, and the solution environment should be changed from acidic to alkaline to avoid the solid precipitation. Figure 3 compares the EDTA solubility at different pH values and concentrations, for solutions prepared using seawater and DI water.

Overall, the concentration of the chelating agents at the specific pH value can be determined utilizing the solubility profiles (Figures 1–3). For certain applications, the required chelating agent can be defined, and then, the solubility curves can be utilized to find the minimum solution pH without inducing solid precipitation. For example, carbonate stimulation is usually performed using 20 wt % EDTA; hence, the pH should be more than 7 to achieve clear and stable solutions, without any solid precipitation. However, for enhanced oil recovery applications, lower EDTA concentrations are used (between 1 and 10 wt %), and the suggested solution pH is around 5–6, to achieve good oil recovery without damaging the reservoir system.

3.2. Properties of Chelating Agents. 3.2.1. Density Models. Na₂EDTA, Na₃HEDTA, and Na₅DTPA solutions were prepared at three various concentrations using DI water. Then, the fluids’ densities were measured at various temperatures. The aim is to establish relationships between the fluid density and the temperature for each chelating agent solution. The density of chelates was measured at temperature ranges from 72 °F to around 175 °F (295.37–352.59 K), and then, the density–temperature curve was extrapolated to 212 °F. Figures 4–6 show the density–temperature relationships of the studied chelating agents at different concentrations. The relationship between the temperature and fluid density was found to be following the polynomial relation of a second order for all the examined chelates. It was found also that changing the pH of the solution of any of these chelates has a negligible effect on their densities. In fact, the density of the chelating agents increased by less than 1% when the pH is increased from 4.5 to 11.5. Figure 7 shows the influence of
fluid pH on the solution density for a 9.25 wt % Na$_2$EDTA chelating agent. Also, it was observed that at a temperature above 150 °F (338.71 K), which is the reservoir temperature for most of the hydrocarbon formations, the difference in the fluid density due to changing the pH is very small (Figures 5–7).

Utilizing the density measurements, empirical correlations can be developed to determine the fluid density for the three chelating agents (EDTA, HEDTA, and DTPA). These equations can relate the density of each chelant to the temperature and the weight concentration of the chelating agents. Three main steps were used to develop the density equations for each chelating agent. First, the density of each chelating agent was plotted versus the chelating agent’s concentration at different temperatures, and each temperature has a separate curve. Second, the best trendline that fits the points for each temperature was determined, and then, the fitting equations were obtained and the constants of each equation were determined. It was found that the relationship between density and temperature can be represented by a polynomial model of second order with three constants. In the last step, each of the three constants of the density equations was plotted versus the temperature to determine the relationship between these constants and the temperature. It was observed that the first-order and second-order variables do not vary much, and hence, they can be simply averaged. However, the third constant showed considerable changes with the temperature; therefore, it is represented as a temperature-dependent function. The developed equations are represented by eqs 1–3. The developed equations can be used to provide quick and reliable estimations for the chelating agent’s density based on the solution concentrations and the working temperatures.

$$\rho_{\text{EDTA}} = -0.00041C_{\text{EDTA}}^2 + 0.01466C_{\text{EDTA}} - 0.000401T + 0.9921$$ (1)
\[ \rho_{\text{HEDTA}} = 0.00008C_{\text{HEDTA}}^2 + 0.00419C_{\text{HEDTA}} - 0.000558T + 1.0663 \]
\[ \rho_{\text{DTPA}} = -0.00009C_{\text{DTPA}}^2 + 0.00862C_{\text{DTPA}} - 0.000569T + 1.0386 \]

where \( \rho_{\text{HEDTA}} \) and \( \rho_{\text{DTPA}} \) are the densities of Na\(_2\)EDTA, Na\(_3\)HEDTA, and Na\(_5\)DTPA in grams per cubic centimeter, respectively, \( T \) is the operational temperature in degrees Fahrenheit, and \( C_{\text{HEDTA}}, C_{\text{DTPA}} \), and \( C_{\text{HEDTA}} \) are the concentrations of Na\(_2\)EDTA, Na\(_3\)HEDTA, and Na\(_5\)DTPA in weight percent, respectively.

The above equations were developed using around 350 measurements and utilizing a multi-fitting approach. The developed equations showed high reliability and gave average errors of around 1% for density estimation, which is acceptable in the oil industry.

Moreover, calcium carbonate at different concentrations was dissolved in 18.5 wt % Na\(_2\)EDTA, 20 wt % Na\(_3\)HEDTA, and 20 wt % Na\(_5\)DTPA chelating agents to develop the relationship between the calcium carbonate concentration and the fluid density. It was found that the chelated calcium ions increased the density of the solution as compared to that of the solution without calcium ions for all the investigated chelants. Utilizing the conducted measurements, new correlations were developed to estimate the fluid density based on the concentration of calcium ions. The equation relating the calcium carbonate concentrations to the density of the final solution can be mathematically expressed as follows
\[ \rho_{18.5\%\text{EDTA}} = 2.6 \times 10^{-6} \times C_{\text{Ca}} - 0.00053 \times T + 1.1404 \]
\[ \rho_{20\%\text{DTPA}} = 4.05 \times 10^{-6} \times C_{\text{Ca}} - 0.00053 \times T + 1.1699 \]
\[ \rho_{20\%\text{HEDTA}} = 2.35 \times 10^{-6} \times C_{\text{Ca}} - 0.00050 \times T + 1.1740 \]

where \( C_{\text{Ca}} \) is the calcium concentration in weight percent.

### 3.2.2 Viscosity Models

The viscosity of chelating agents is very crucial in the design of matrix stimulation treatment. Chelating agents’ viscosity is needed to calculate and model the pressure drop during the treatment. The pressure drop is very important to calculate the pumping requirements of the system. The viscosity drop is needed to calculate and model the pressure drop during the treatment. The pressure drop is very important to calculate the pumping requirements of the system.

Empirical equations were developed based on the experimental results (Figure 8–10) that relate the chelating agent viscosity to both temperature and concentration. Similar to the density equations, three main steps were adopted to develop the viscosity equations of the chelating agents. At the first step, the viscosity of the chelating agent was plotted versus the chelating agent’s concentration at different temperatures, and each temperature has a separate curve. Second, the best trendline that fits the points for each temperature was determined; the fitting equations were obtained; and the constants of each equation were determined. It was found that the relationship between temperature and fluid viscosity can be captured using an exponential model of two constants. At the last step, the two constants of each equation were plotted versus the temperature to determine the relationship between these constants and the temperature. It was observed that the two constants have a power-law relationship with the temperature; therefore, these constants were represented as temperature functions in the general viscosity equation. The developed equations that can be utilized to determine the chelating agents’ viscosity based on the temperature and concentration are...
μ = × × − × × −

T

93.8947 e

EDTA

1.1113 (0.0821 ) EDTA

0.1206

(7)

μ = × × − × × −

T

78.7890 e

HEDTA

1.0692 (0.0684 ) HEDTA

0.0978

(8)

μ = × × − × × −

T

96.5460 e

DTPA

1.1180 (0.1498 ) DTPA

0.1675

(9)

where μEDTA, μDTPA, and μHEDTA are the viscosities of Na2EDTA, Na2DTPA, and Na2HEDTA chelating agents in centipoise, respectively, C is the chelating agent concentration in weight percent, and T is the temperature in degrees fahrenheit.

Equation 7–9 can be applied to determine the viscosity of the chelating agent when the solution concentrations and temperature are identified. Equation 7–9 gave an average absolute error of 2%. Also, one can note that at a high temperature above 175 °F (352.59 K), this error can be neglected because at high temperatures, the viscosity values are small (Figure 11).

Calcium carbonate at different concentrations was dissolved in 18.5 wt % Na2EDTA, 20 wt % Na3HEDTA, and 20 wt % Na5DTPA chelating agents to develop the relationship between the calcium ion concentration in the chelant and the fluid mixture’s viscosity. It was found that increasing the chelated calcium ions (Ca2+) can lead to the increase in the solution viscosity, for all chelant types. From these tests, we found that the equation relating the Ca2+ concentration to the viscosity of the final solution can be mathematically expressed as follows

μEDTA = 93.8947 × T−1.1113 × e(0.0821 × CEDTA × T−0.0821)

(7)

μHEDTA = 78.7890 × T−1.0692 × e(0.0684 × CHEDTA × T−0.0684)

(8)

μDTPA = 96.5460 × T−1.1180 × e(0.1498 × CDTPA × T−0.1498)

(9)

3.2.3. Interfacial Tension. The IFT was measured for Na2EDTA and Na3HEDTA solutions prepared at various concentrations. The IFT measurements aimed to determine the interfacial forces at the interface between the oil droplet and the chelating agents. The chemical concentration was changed to investigate its effect on the IFT values. Table 2

Table 2. Properties of Chelants Used in IFT Tests

| chelating agents | concentration, wt % | solution pH |
|------------------|---------------------|-------------|
| EDTA             | 20                  | 8           |
|                  | 15                  | 8           |
|                  | 10                  | 8           |
| HEDTA            | 20                  | 4           |
|                  | 15                  | 4           |
|                  | 10                  | 4           |

Figure 9. Viscosity of Na2DTPA at different temperatures and chelant concentrations. The markers indicate the experimental results, and the solid line indicates the predicted values obtained using the developed models. The fluid viscosity was reduced with the increasing temperature.

Figure 10. Fluid viscosity for Na3HEDTA at different temperatures and chelant concentrations. The markers indicate the experimental results, and the solid line indicates the predicted values obtained using the developed models. Reducing the chemical concentration led to the reduction of the fluid viscosity at all temperatures.

Figure 11. Fluid viscosity for 9.25 wt % Na2EDTA at different pH values as a function of temperature. The markers indicate the experimental results, and the solid line indicates the predicted values obtained using the developed models. A viscosity difference of 0.55 cP was obtained at room temperature, and almost the same viscosity values were obtained at high temperatures.
shows the chelating agent’s properties. Crude oil samples having API gravities of 31.2, 35.6, and 40.0° API were used, and chemical concentrations of 10, 15, and 20 wt % were examined to understand the effect of chelating agent concentrations on the IFT. The experiment was carried out under ambient conditions.

Figure 12 shows the relationship between the IFT of Na₂EDTA–crude oil and the density of the crude oil at different chelating agent concentrations. From Figure 12, it is clear that IFT decreases as crude oil becomes lighter. This can be attributed to the reduction in the oil density and weakness in the electrical interaction. The same trend was obtained when the concentration of the chelating agent was changed. When the chelating agent’s concentration was decreased, IFT was also decreased for the same crude oil density. Moreover, Figure 13 illustrates the relationship between oil density and interfacial forces using different concentrations of Na₃HEDTA. As shown in Figure 13, the oil density showed little effect on the IFT; almost the same IFT values were obtained at different API gravities for each Na₃HEDTA concentration.

![Figure 12](https://example.com/fig12.png)

**Figure 12.** Interfacial force at the oil/Na₂EDTA interface for various concentrations (10, 15, and 20 wt %) and API gravities (31–40° API).

![Figure 13](https://example.com/fig13.png)

**Figure 13.** Interfacial force at the oil/Na₃HEDTA interface for various concentrations (10, 15, and 20 wt %) and API gravities (31–40° API).

Overall, the decrease in chelate concentration can lead to a considerable reduction in the IFT at the same oil density. However, slight changes in the IFT were observed for different oil densities at the same chelating agent concentration, suggesting that the forces at the chelating agent/oil interface surface are affected mainly by the chelant concentration rather than the density of crude oil.

### 3.3. Carbonate Stimulation Using the Optimized Chelating Agent Solutions

Two acidizing treatments were conducted to improve the permeability for tight carbonate rocks by creating continuous wormholes along the treated cores. The optimized chelating agent solutions were used to create wormholes using the minimum required acid volume. Figure 14 presents CT scan images for carbonate rocks after acidizing treatment, where clear wormholes across the cores can be seen for both samples. It should be noted that sample A was treated with 20 wt % HEDTA, while 15 wt % HEDTA solution was used to treat sample B. During the acidizing treatments, the pressure drop profiles across the rock samples were obtained as shown in Figures 15 and 16. Generally, the pressure drop changes based on the acid penetration within the rocks and the growth of wormholes. In the beginning, the pressure drop increases because of the chelating agent viscosity; the injected acids have higher viscosity than the KCl brine inside the rock samples. Also, the injected acid dissolves part of the carbonate matrix, leading to higher viscosity. Moreover, the creation and growth of wormholes within the treated rocks lead to a reduction in the pressure drop because the induced wormholes increase the total rock permeability. Eventually, the pressure drop decreases to around 1.5 psi (0.01 MPa) when the wormhole is formed along the rock sample.

![Figure 14](https://example.com/fig14.png)

**Figure 14.** CT images for two carbonate rocks after injection of HEDTA acid, where core A is treated with 20 wt % HEDTA, while core B is treated with 15 wt % HEDTA.

### 3.4. Prediction of Pressure Drop and Acid Volume

The developed eqs 1–12 were used to assist in predicting the required pore volume of acid to achieve the breakthrough, as well as predicting the pressure drop during the acid injection. The chelating agent’s physical properties were estimated using the developed equations (eqs 2, 6, and 8) under the experimental conditions. The model proposed by Mahmoud and Nasr-El-Din⁴⁰ was adopted to estimate the required acid volume. The injected acid volume that is required to create a continuous wormhole was predicted. Also, the developed...
equations were incorporated with Darcy’s equation to predict the pressure drop during the chelating agent flooding into the carbonate rocks. A considerable reaction between the carbonate matrix and the injected chelating agent is expected, which can lead to a significant increase in the calcium ions in the solution; therefore, the fluid density was adapted accordingly, using eq 12. The modified equation for estimating the pressure drop during acidizing treatment using chelating agents is given by

\[
\Delta p = \frac{122.8Q\mu_{\text{chelate}}(L_{\text{chelate}} - L_{\text{wh}})}{kd_{\text{core}}^2} + \frac{122.8Q\mu_{\text{water}}(L_{\text{core}} - L_{\text{chelate}})}{kd_{\text{core}}^2}
\]  

(13)

where \(\Delta p\) is the pressure drop in pounds per square inch, \(Q\) is the injection rate in cubic centimeters per minute, \(\mu\) is the fluid viscosity in centipoise, \(k\) is the initial core permeability in millidarcy, \(L_{\text{chelate}}\) is the core length saturated with the chelating agent, and \(L_{\text{chelate}}\) and \(L_{\text{core}}\) are the lengths of the chelating agent and core, respectively.

**Figure 15.** Pressure drop profile during the injection of 20% HEDTA into a tight carbonate sample (core A).

**Figure 16.** Pressure drop profile during the injection of 15% HEDTA into a tight carbonate sample (core B).

**Figure 17.** Profiles of pressure drops (actual and predicted) during carbonate acidizing using 20 wt % HEDTA and an injection rate of 0.5 cm³/min. An estimation error of 9.7% was obtained between the predicted and actual pressure drops.
agent in inches, $L_{wh}$ is the generated wormhole length in inches, $L_{core}$ is the total core length in inches, and $d_{core}$ is the core diameter in inches.

The pressure drop across the sample is basically determined by summing the pressure drop for the part of the core that is saturated filled with the chelating agent (can be defined as the swept part) and the part of the rock that not reached by the acid (nonswept part). Within the swept part, a wormhole is generated due to the interaction between the injected acid and carbonate matrix; however, no wormhole was induced in the nonswept part. Upon injecting more acid, the wormhole (and the swept part length) will continue growing till reaching the end side of the treated rock sample; hence, the swept part length ($L_{chelate}$) will equal the total core length ($L_{core}$). It should be noted that the pressure drop inside the wormhole is very small, and thus, it can be neglected. Also, the developed pressure drop equation (eq 13) implies a single-phase flow, which can be particularly achieved by increasing the back-pressure to ensure full solubility of any gases generated during the acid/carbonate reaction. It should be emphasized that all properties during the carbonate acidizing were estimated using the developed equation, and then, the pressure drop was predicted. Figures 17 and 18 show the profiles for the pressure drop during two carbonate acidizing experiments; the predicted pressure drop during the experiments are provided and compared with the measured pressure drop during the carbonate treatments. A good agreement between the actual and predicted pressure drops can be observed, and the estimation error is around 7.2%.

4. CONCLUSIONS

A comprehensive study was conducted for widely used chelating agents to determine their solubilities and fluid properties at different temperatures, calcium ion concentrations, and chelant concentrations. EDTA, DTPA, and HEDTA chelating agents of sodium bases were used and prepared using seawater and DI water. The following conclusions were drawn from this study:

- $\text{Na}_2\text{DTPA}$ and $\text{Na}_3\text{HEDTA}$ chelating agents are soluble in the pH range from 2 to around 13 for all the investigated concentrations up to 40 wt % without any precipitation.
- The $\text{Na}_2\text{EDTA}$ chelating agent has limitations in solubility due to the effect of solution pH. EDTA solutions should be prepared at a pH higher than 7.5% to avoid solid precipitation.
- Among the three chelating agents, $\text{Na}_2\text{DTPA}$ and $\text{Na}_3\text{HEDTA}$ are good stimulation fluid candidates for offshore operations where freshwater is difficult to be secured. $\text{Na}_3\text{HEDTA}$ is highly recommended since it is environmentally friendly.
- New models proposed to estimate the density and viscosity of chelating agents’ solutions at various temperatures, calcium ion concentrations, and chelant concentrations have been empirically developed.
- The solution pH has a negligible effect on the chelant’s density. On the other hand, the pH has a noticeable effect on the chelant’s viscosity, but at temperatures higher than 175 °F (352.59 K), its effect can be neglected.
- The developed equations can be used to determine the density and viscosity of the specified chelating agent at any temperature and concentration values with very acceptable errors.
- The developed correlations of chelating agents’ fluid properties helped in matching the pressure drop during the stimulation treatment of carbonate rocks.

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Figure 18. Profiles of pressure drops (actual and predicted) during carbonate acidizing using 15 wt % HEDTA and an injection rate of 1 cm$^3$/min. An estimation error of 4.6% was obtained between the predicted and actual pressure drops.
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Notes
The authors declare no competing financial interest.

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