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Modeling the Impact of Wettability Alterations on Calcium Carbonate System for Crude Oil and Asphaltenic Solutions

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ABSTRACT: This study demonstrates a novel approach to examine the wettability tendency on calcium carbonate using zeta potential measurements. Different crude oil samples and asphaltenic solutions were studied and wettability profiles of limestone for these fluids were obtained using the zeta potential technique. In this study, suitable models (using Mathematica 8 and MS Excel) have been examined in order to fit the obtained data to the corresponding wettability profiles. A logistic model and a cycloid model were considered to represent the wettability profiles of limestone for crude oil and asphaltenic solutions, respectively. The R-squared value for the logistic function fit was found to be 0.99 with a standard deviation of 0.61 and a relative error of 1×10^{-3}%. For the cycloid model, the best fit to the wettability profile for asphaltenic solutions, with different concentrations of 0.625, 1.25, and 2.5 wt %, were found to have an R-squared value ranging 0.86−0.98 with a maximum relative error of 1.33%.

1. INTRODUCTION

With advancement in technology and increasing scarcity of resources, modeling has gained recognition over time. Nearly all fields of study use models to assist them in understanding phenomena related to their topic of interest. In the petroleum industry, during production, various problems such as well-bore plugging, pipeline deposition, sedimentation, and plugging during crude oil storage occur.[1] Wettability of the reservoir rock is a tendency phenomenon that helps in understanding such problems.[2] In addition to performing wettability experiments, researchers have modeled the wettability alteration process a reservoir rock undergoes.[3] These developed models not only aid in strengthening mechanistic understanding of the process but also help in predicting the wettability variation.[4]

Wettability models have been developed previously based on experimental data obtained from contact angle measurements, or relative permeability method or imbibition experiments.[3−5] Various relative permeability and capillary pressure curves that correspond to different wetting states were used to model the wettability alteration.[3] This study aims to fit primitive models for the wettability profiles of calcium carbonate, for crude oil and its asphaltenic component, obtained using zeta potential measurements. These fitted models would assist in determining the current state of wettability by zeta potential measurements. In addition, the models would help predict the concentration of oil at which the wettability of the rock would alter.

2. MATERIALS AND METHODS

This section discusses the experiments conducted in order to generate the wettability curves. Moreover, the models examined and the modeling approach used in order to fit to the wettability profiles are stated, in detail.

2.1. Experimental Section. The zeta potential technique is a novel method to measure wettability and study the wettability alteration of a reservoir rock with the help of zeta potential measurements.[6] By using this technique, wettability profiles can be generated that indicate the transition of reservoir rock surface wetness, from water-wet to oil-wet.[6,7] Figures 1 and 2 show the wettability profiles of calcium carbonate resulted from wettability experiments, using the zeta potential technique, for crude oil and asphaltenic solution of varying concentration, respectively.

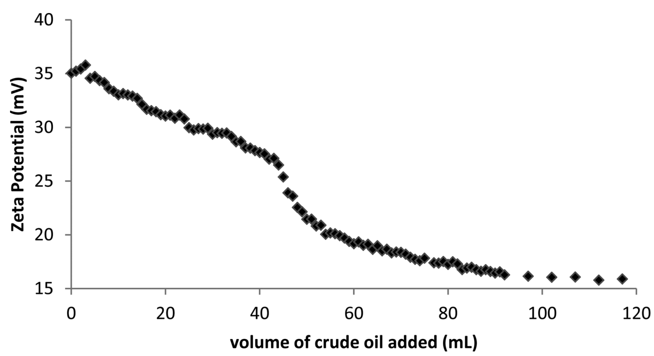

Figure 1. Wettability profile of calcium carbonate for crude oil at RTP.[6]

As evident from Figure 1, the initial zeta potential value is observed to be around +35 mV for limestone in water. By adding crude oil, the zeta potential is seen to decrease steadily until about 45 mL of crude oil has been added to the limestone−water mixture. A sharp decrease is evident over the approximated range 45−50 mL. The zeta potential decreases further steadily until a plateau is reached. In all, the wettability profile of limestone for crude oil appears to be an "S" shaped smooth curve, flipped horizontally.

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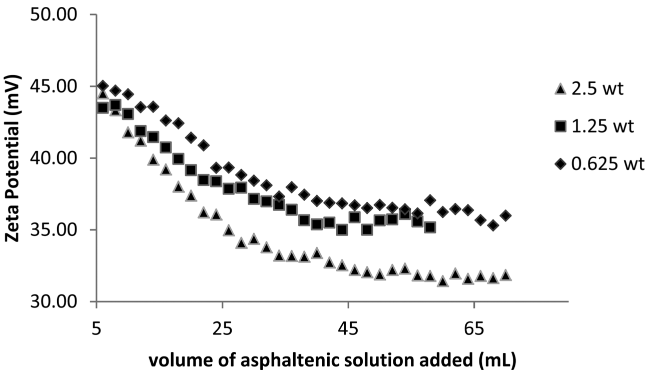

Figure 2. Wettability of aqueous limestone mixture for asphaltenic solutions varying the concentrations of crude oil at RTP.[7]

As seen in Figure 2, the zeta potential is observed to decrease exponentially upon the addition of the asphaltenic solutions, for all concentrations. However, the profiles tend to differ in the region indicated by the plateau. The solutions used in this experiment comprised *n*-heptane insoluble asphaltene and toluene. The solution with the highest asphaltene content is observed to reach the highest negative zeta potential value. On the other hand, the solution with the least asphaltene content is observed to reach the lowest negative zeta potential value. Hence, the asphaltene content can be safely assumed to be the reason behind the difference in the trend.

2.2. Examined Models. There are several models that can be considered for fitting to each of the obtained wettability profile. Below are the models, with relevant background, that are chosen in this study.

2.2.1. Logistic Model. A logistic curve is an S-shaped (sigmoidal) curve that serves as a suitable mathematical model for describing many natural phenomena.[8] It has been widely used in studies pertaining to population growth.[9] Nevertheless, Reed and Berkson[10] demonstrated its application to experimental data for several chemical reactions several decades ago.

The logistic growth function can be represented by the following equation

$$f(t) = \frac{A}{1 + Be^{-kt}} \tag{1}$$

where A, B and k are positive constants.

2.2.2. Cycloid Model. The cycloid model is defined kinematically, as the plane curve traced by a point on a circle rolling along a straight line.[11] There are several properties of the cycloid model, such as tautochrone, isochrone, and brachistochrone, which make it useful for various fields of natural sciences.[11,12]

The x-coordinate of the cycloid can be represented by

$$x = r(\theta - \sin\theta) \tag{2}$$

whereas the y-coordinate of the cycloid can be represented by

$$y = r(1 - \cos\theta) \tag{3}$$

where r is the radius of the circle, forming the cycloid, and θ is the angle, in radians, that defines the length of the cycloid.

Exponential and logarithmically decreasing models have also been analyzed for fitting the wettability profiles. However, the logistic and cycloid models are the best fits for the data respectively and hence, the focus of our study.

2.3. Modeling Approach. Wolfram Mathematica 8 and Microsoft Excel 2007 were used as tools to find the best fitting for the wettability profiles, obtained using the zeta potential technique.

2.3.1. Wettability of Calcium Carbonate for Crude Oil. As evident from the wettability profile of crude oil, shown in Figure 1, the experimental data forms an S-shaped curve, reflected about the x-axis. From the reviewed literature, the logistic (sigmoidal) function is seen to conveniently fit such curve.[13] The exponential function can be used along with the learning curve. However, as mentioned earlier, the logistic curve encompasses the properties of both functions while being smooth. In addition, logistic functions lead to more efficient

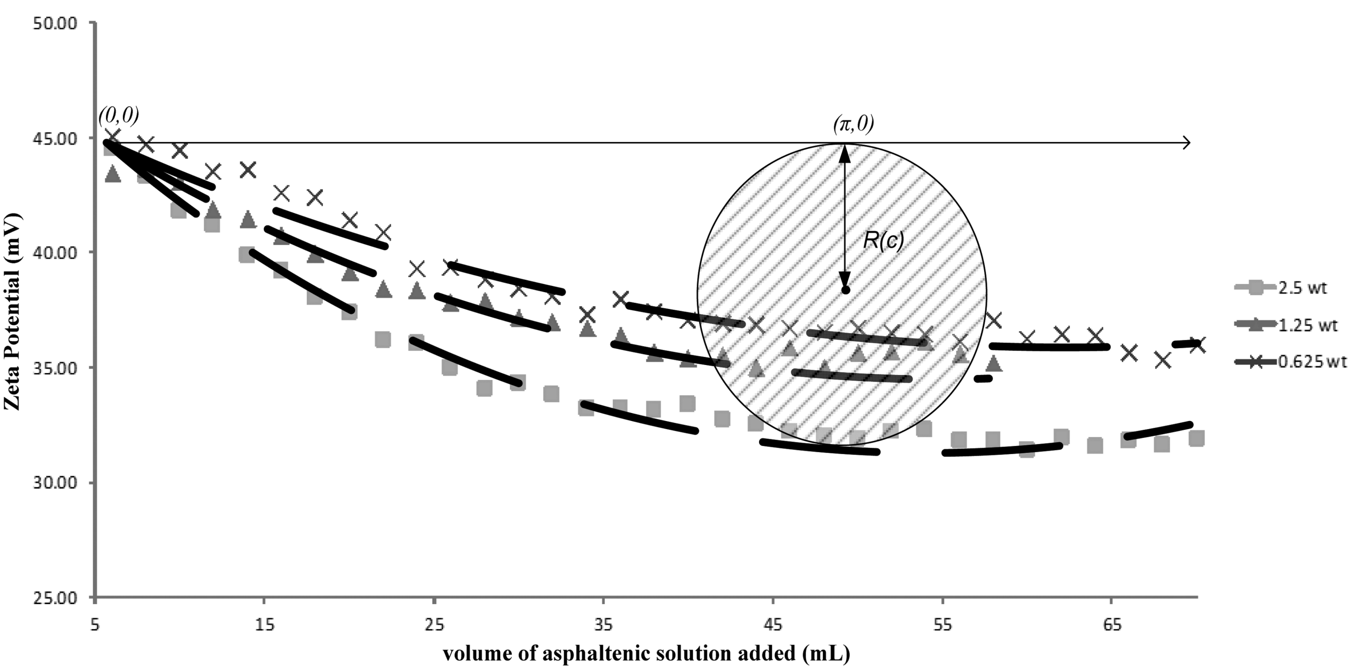

Figure 3. Illustration of the apparent cycloid structure in the experimental data obtained.

estimation of models.[13,14] Numerous studies have been conducted in different fields where logistic curves have been used. Moreover, they have been compared with other statistical models and are regarded as the best fit models in terms of sensitivity and prediction.[13−15]

The logistic function, in its most general form, expressed in eq 4, was used as a trial model of the function while carrying out nonlinear regression.

$$f(t) = \frac{-A}{1 + Be^{-kt}} \tag{4}$$

Wolfram Mathematica 8 was used to fit the model to the data set. The equation was entered into the software to determine the constants based on regression. The model was modified with each try to obtain a fit with the smallest deviation from the wettability profile. Based on trial and error, the best fit was obtained.

2.3.2. Wettability of Calcium Carbonate for Asphaltenic Solutions. From observation, the results obtained from the wettability profile of calcium carbonate for asphaltenic solutions showed structures that can be best characterized by a cycloid model of varying radii, as illustrated in Figure 3.

As stated earlier, the cycloid encompasses numerous properties that make it an appropriate choice as compared to other statistical models. According to the data set, it is noted that the concentrations of the asphaltenic solutions have an effect on the volume of asphaltenic solution added (x) and the zeta potential (y) parameters of the curve. As opposed to other statistical models, the cycloid model can be easily developed to fit both parameters simultaneously without any degree of complexity.

A relationship was obtained between the radius of the circle forming the cycloid and the concentration, as shown in Figure 4.

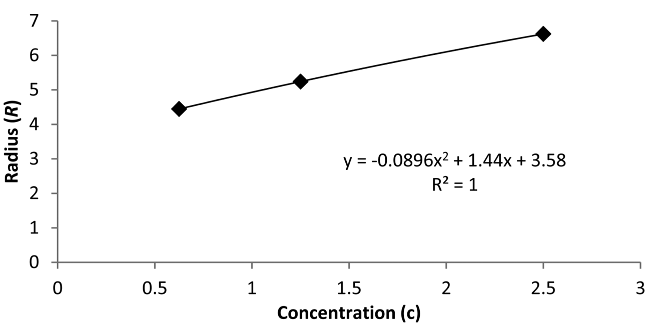

Figure 4. Graph of concentration (c) vs radius (R).

As evident from Figure 3, the height of the cycloid equals twice the radius of the circle, forming the cycloid. Therefore, the height of each cycloid, distance from the initial point to the beginning of the plateau, was measured and divided by 2. This was plotted for each set of data set versus their concentration, as seen in Figure 4. The function that best fit the data is expressed by eq 5.

$$R(c) = -0.0896c^2 + 1.44c + 3.58 \tag{5}$$

The above function was incorporated to the Cartesian functions that define the cycloid, as follows:

$$x = (-0.0896c^2 + 1.44c + 3.58)(\theta - \sin\theta) \quad 0 \le \theta \le \pi$$

$$y = (-0.0896c^2 + 1.44c + 3.58)(1 - \cos\theta) \quad 0 \le \theta \le \pi$$

The function runs for θ from 0 to π, so that it forms a half cycloid. Additionally, the function needed to resized and adjusted along the axes in order to best fit with the experimental data. Hence, the overall function resulted as follows:

$$x = 6 + \left(\frac{60(t - \sin(t))}{\pi}\right)$$

$$y = 45 - (-0.0896c^2 + 1.44c + 3.58)(1 - \cos(t))$$

For conversion from unit-less to milliliters, the x-coordinate was multiplied by a factor of $60/(R(c) \times (\pi - \sin\pi))$. Based on the experimental data, the cycloid curve extends over an average period of 60 mL, from 6 to 66 mL while θ_{max} equals π. Therefore, the function was divided by $R(c) \times (\pi - \sin\pi)$. Additionally, the x-coordinate was increased by a factor of 6 to shift the cycloid 6 units to the right, since the fall in the experimental data is apparent after a volume addition of 6 mL.

The y-coordinate was initially in units of voltage. However, it was inverted by multiplying it by −1 and adjusted by increasing it by 45 mV so that it appears within the range of the experimental data.

3. RESULTS AND DISCUSSION

The examined models were fit to the wettability profiles of calcium carbonate for crude oil and for asphaltenic solutions of different concentrations. The residuals have been calculated to show the deviation of the model from the experimental data.

3.1. Wettability of Calcium Carbonate for Crude Oil. Figure 5 shows the results obtained from the model as compared to the experimental data for the zeta potential measurements of calcium carbonate, as crude oil is added.

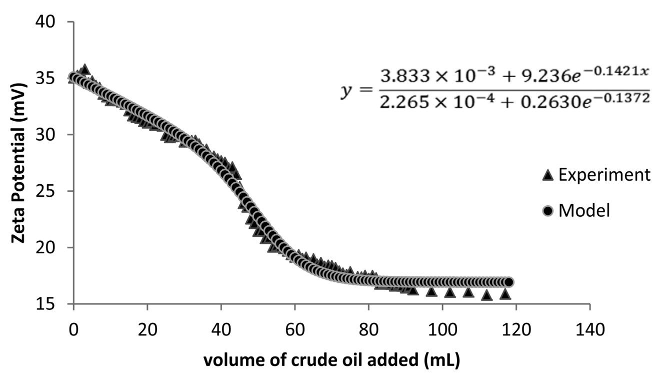

Figure 5. Comparison between the experimental data and the results obtained from the model for wettability profile of calcium carbonate for crude oil.

The final logistic function that represents the model shown in Figure 5 is

$$y = \frac{3.833 \times 10^{-3} + 9.236e^{-0.1421x}}{2.265 \times 10^{-4} + 0.2630e^{-0.1372}} \tag{6}$$

3.1.1. Measure of Fitness of the Model. There are several ways to measure the fitness of a model to the experimental data. The deviation of the logistic model from the experimental data can be determined by calculating the R-squared value. Like the R^2 value obtained from linear regression or correlation analyses, the R^2 value can range from 0 to 1; proximity to 1 indicates the proximity with which the model fits the data set.[14]

For this logistic function, the calculated value for R^2 was found to be 0.99 which indicates a very good fit to the experimental data. By observation, it can be seen that the logistic (sigmoid) model follows the same trend as the experimental data. There is a steady fall in the zeta potential value observed in the beginning, followed by a steep fall and a plateau. The plateau, however, deviates from the experimental value. Moreover, the curve appears to be smoother than the experimental curve. The standard deviation was found to be 0.61 whereas the relative error was calculated to be 1×10^{-3}%. In all, these statistical tools indicate the model results in a good fit.

3.2. Wettability of Calcium Carbonate for Asphaltenic Solutions. The following subsections discuss the results obtained from the model as compared to the experimental data for the wettability profile of calcium carbonate for asphaltenic solutions of concentrations 0.625, 1.25, and 2.5 wt %.

3.2.1. Model Fitted for 0.625 wt % Asphaltenic Solution. Figure 6 shows the data comparison between the model and experiment.

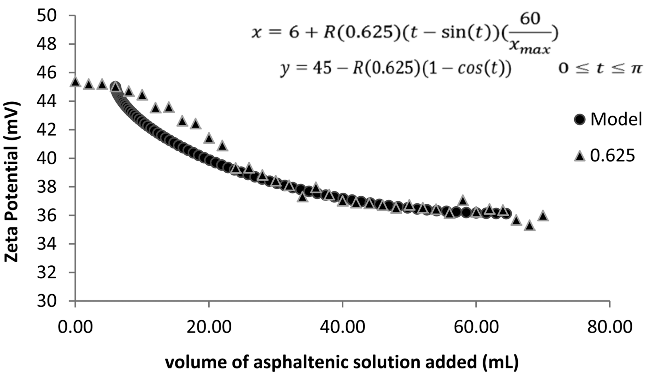

Figure 6. Comparison between the experimental data and the results obtained from the model for wettability profile of calcium carbonate for 0.625 wt % asphaltenic solution.

The calculated R-squared value was found to be 0.86 which indicates a good fit of the model. The standard deviation was calculated to be 0.79 with a relative error of 1.33%.

3.2.2. Model Fitted for 1.25 wt % Asphaltenic Solution. Figure 7 shows the data comparison between the model and wettability experiment for 1.25 wt % asphaltenic solution.

The calculated R-squared value was found to be 0.96 which indicates that the model is in good agreement with the experimental data. The standard deviation was calculated to be 0.57 with a relative error of 0.76%.

3.2.3. Model Fitted for 2.5 wt % Asphaltenic Solution. Figure 8 shows the data comparison between the model and experiment for 2.5 wt % asphaltenic solution.

The calculated R-squared value was found to be 0.98 which indicates a very good fit of the model. The standard deviation was calculated to be 0.50 with a relative error of 0.63%.

4. CONCLUSION AND RECOMMENDATIONS

Adequate types of models were fit to the wettability profiles of limestone for crude oil and asphaltenic solutions of varying concentration. The equations produced were best fit to the data. The model fits were assessed by statistical tools and were found to be in good agreement with the experimental data. It is observed from the results that the model tends to fit better for solutions of higher asphaltene content. Moreover, it can be seen in Figure 6, for 0.625 wt % asphaltenic solution, that deviation of the model from the experimental data at the beginning is quite significant as compared to that of 1.25 and 2.5 wt % solutions. A probable reason for this behavior could be a result of the lower magnitude of negative charge induced by the asphaltene molecules in limestone−water mixture for 0.625 wt % asphaltenic solution. As seen from Figure 2, the zeta potential decreases as asphaltenic solutions are added to the mixture. When the concentration of the asphaltenic solution is increased, the zeta potential falls to a lower zeta potential value. In the case of 0.625 wt % asphaltenic solution, the decrease is relatively gradual as compared to the 1.25 and 2.5 wt % asphaltenic solutions, due to its lower concentration. It takes a higher volume of asphaltenic solution addition to lower the zeta potential value for lower concentration as opposed to higher. Hence, a greater deviation is observed, as indicated by the standard deviation and relative error values.

Other models such as exponential and logarithmically decreasing functions can be further studied. In addition, the DLVO model may be considered with focus on the van der Waals forces of attraction. Nevertheless, the logistic function and the cycloid model, presented in this study, serve as a stepping stone for researchers with the aim of modeling the

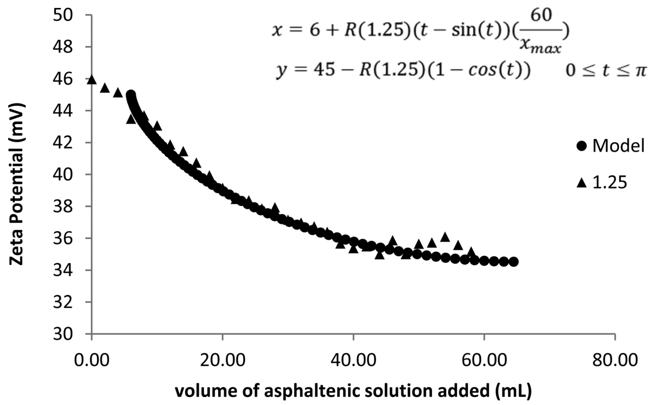

Figure 7. Comparison between the experimental data and the results obtained from the model for wettability profile of calcium carbonate for 1.25 wt % asphaltenic solution.

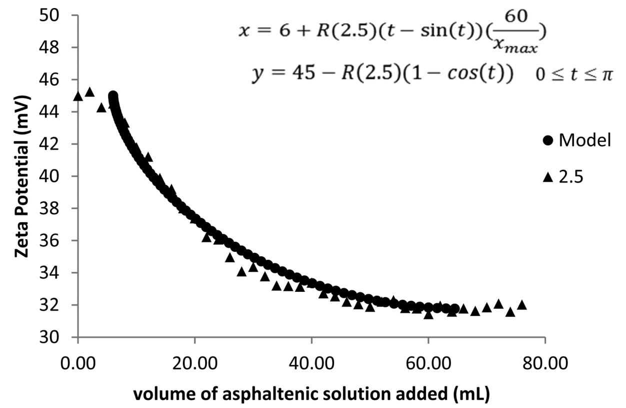

Figure 8. Comparison between the experimental data and the results obtained from the model for wettability profile of calcium carbonate for 2.5 wt % asphaltenic solution.

wettability profile obtained through zeta potential measurements. Further studies can be carried out with different operating conditions and the effects can be incorporated into the models. Such models can then be used to predict system behavior at different conditions.

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Notes

The authors declare no competing financial interest.

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