

Impact of calcium citrate precipitation on the reaction of citric acid-calcite

M.H. AlKhalidi ^{a,*}, H.A. Nasr-El-Din ^b, H. Sarma ^a

^aThe University of Adelaide, Adelaide, SA 5005, Australia

^bTexas A&M University College Station, Texas 77843

Abstract

Mass transfer process during the reaction of citric acid with calcite was investigated using the rotating disk apparatus. The effects of disk rotational speed and temperature on the diffusion coefficient of citric acid were examined.

Using the rotating disk apparatus, the calcite dissolution in 7.5 wt% citric acid solutions was measured at different temperatures, (25, 40, 50°C). The reaction of citric acid with calcite is mainly dependent on disk rotational speed, and the temperature value. For example, at 50°C, the reaction is mass-transfer limited at 500 rpm, while it is reaction-limited below these rotational speeds. Calcium citrate formation is also dependent on the rotational speed. More calcium citrate forms at high rotational speeds.

The effective diffusion coefficient of citric acid was calculated based on the rotating disk theory. The effective diffusion coefficient of citric acid was found to be a function of the interplay between the calcium citrate precipitation and the presence of the counter calcium ions. At an initial acid concentration of 7.5 wt%, the effects of calcium citrate precipitation and counter calcium ions were significant and the reported citric acid diffusion coefficients were not comparable with its measured effective diffusion coefficients using the rotating disk. The effect of temperature on the diffusion coefficient of citric acid at a constant citric acid concentration was found to follow Arrhenius law, and the activation energy is equal to 37.9 kJ/mol.

Keywords: citric acid; calcite; dissolution rate, mass transfer, diffusion, rotating disk

Corresponding Author

E-mail address: mohammed.alkhalidi@student.adelaide.edu.au

Introduction

Over the last few years, various acid systems, such as gelled acids, viscoelastic surfactants-based acids (VES), emulsified acids, and encapsulated citric acid, have been introduced to address some of the concerns with HCl such as severe corrosion problems and poor etched fracture lengths (Crowe et al., 1988). Except of citric acid system; these acids have been extensively studied and successfully employed in acid fracturing treatments (Nasr-El-Din et al., 2006; Al-Mohammad et al., 2006; Al-Al-Mutairi et al., 2007; Nasr-El-Din et al., 2008; Mutairi et al., 2008).

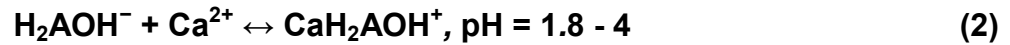
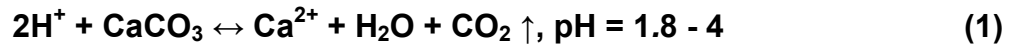
Citric acid was introduced because it can be used in an encapsulated form, which prevents its reaction with both the production tubulars and the formation up to 180°F (Blauch et al., 2003; Burgos et al., 2004), and hence this will protect well tubulars, and those made of corrosion resistant alloys from strong and corrosive acids, especially at high temperatures. This use of encapsulated citric acid in petroleum fields has met with mixed field results. Blauch et al. (2003) reported positive field results and that the formation damage because of calcium citrate precipitation was not a major concern at down-hole conditions. However, Burgos et al. (2004) reported that there was no improvement in the performance of an acid-fractured well after the application of encapsulated citric acid. They explained the unexpected field results in terms of calcium citrate precipitation. These mixed field results highlighted that a better understanding of the reaction of citric acid with calcite is needed.

Previous studies have investigated the reaction of citric acid with calcite. Using the rotating disk apparatus, these studies have shown that the reaction is mainly limited by the mass transfer process and the calcium citrate precipitation plays an important role in the reaction of citric acid with calcite. However, these studies have been conducted over very limited range of parameters (Alkhaldi et al., 2005; Alkhaldi et al., 2007).

In order to design an effective acid fracturing treatment, it is essential to know the effective diffusivity of the acid system at different field conditions, which is needed to determine the geometry of the fracture. Therefore, the objectives of this study are to: (1) measure the calcite dissolution rate using the rotating disk apparatus over a wide range of parameters and (2) investigate the effect of temperature on the overall mass transfer coefficient.

Chemistry of citric acid and precipitation of calcium citrate

The reaction of citric acid with calcite at pH values of 1.8 to 4 is as follows:



According to Alkhalidi et al. (2005), precipitation of calcium citrate complexes occurs at low pH values of nearly 3.0. If calcium citrate precipitates during the reaction, it will form a layer on the calcite surface and then it will act as a diffusion barrier, which will slow the overall mass transfer process. Therefore, it is very important to examine the surface of the calcite disk at the end of each experiment to determine whether calcium citrate precipitated during the citric-calcite reaction or not.

Mass transfer into a rotating disk in reactive environments

The calcite-citric reaction can be described by the following three steps: (1) the transport of citric acid molecules to the solid surface, (2) the dissociation of citric acid and the reaction at the surface, and (3) the transport of products away from the interface. The overall reaction rate is determined by the slowest step.

In the diffusion-limited regime, the mass transfer flux of a specie i , J_i , can be expressed in terms of the concentration of the transferring specie, and the mass transfer coefficient, k_{mti} , as follows:

$$J_i = k_{mti} (C_{Bi} - C_{Si}) \quad (4)$$

where C_{Bi} is the concentration of specie i in the bulk solution, and C_{Si} is its concentration at the surface of the disk. The mass transfer coefficient in Newtonian fluids, is a function of the effective diffusion coefficient of specie i , physical properties of the solution, and the square root of the rotational speed. It can be determined under laminar flow conditions ($Re \leq 3 \cdot 10^5$ and $Sc > 100$) using **Equation 5** (Levich, 1962; Newman, 1966):

$$k_{mt} = \frac{(0.62048) (Sc)^{-2/3} (\sqrt{\omega \nu})}{1 + 0.2980 (Sc)^{-1/3} + 0.14514 (Sc)^{-2/3}} \quad (5)$$

where Sc is Schmidt number (v/D), Re is Reynolds number ($\omega \cdot R^2/v$), v is the kinematic viscosity of specie i solution, D is the effective diffusion coefficient of specie i , ω is the disk rotational speed, and R is the calcite disk radius.

Experimental studies

The experimental procedure reported by Alkhaldi et al. (2007) was used to conduct this study.

Results and discussion

Calcium citrate precipitation

Calcite disks reacted with different citric acid solutions for 50 minutes at 50°C were examined. The reacted disks were analyzed by scraping the surface with a spatula and running XRD analysis on the collected solids. The results showed that the scrapped solids contained a mixture of calcium citrate tetra-hydrate and calcium carbonate. Due to calcium citrate precipitation, it was expected that the pH value of the bulk solution to be above 3.0, based on **Equations 1-3**. However, the maximum increase in the pH value of the bulk solution was measured at 7.5 w% at 50°C, where the pH increased from 1.8 to 2.3 due to the reaction, but no precipitate was noted in the solution.

The pH at the reaction interface is expected to exceed 3.0 based on the fact that calcium citrate precipitate was noted at the reacted calcite disk.

Calcite dissolution in citric acid solutions

Figure 1 shows the dissolution rate of calcite in citric acid solutions of initial concentrations of 7.5 wt% as a function of the reaction temperature at rotational speeds of 100 to 1,000 rpm and 1,000 psi. The dissolution rate of calcite is proportional to the square root of the rotational speed from 100 to nearly 500 rpm. Hence, the reaction of citric acid with calcite is mass-transfer limited. The plateau portion, from 500 to 1000 rpm, suggests that the dissolution rate is limited by the surface reaction rate because the dissolution rate remained constant when the disk rotational speed was doubled (Lund et al., 1975). In addition, it was found that the increase in temperature resulted in higher dissolution rate, as expected. However, it is evident from the data that temperature has a significant effect on the calcite dissolution in the reaction-limited regime when it is compared to its effect in the

mass-transfer-limited regime. This is mainly due to the strong dependence of the reaction rate constant on temperature (Schmidt, 1998). In general, log of the rate constant of any chemical reaction has a linear relationship with the inverse value of the reaction temperature.

The effective diffusion coefficient of citric acid

The diffusion coefficient of citric acid at 7.5 wt% is $5.9E - 6 \text{ cm}^2/\text{s}$ (Levien, 1955) at 50°C . The pH value under these conditions was measured in the present study and found to be 1.8. The diffusion coefficient calculated using the data given in **Figure 1** was found to be $4.5E-6 \text{ cm}^2/\text{s}$ at 50°C and $\text{pH}_{\text{solution}} = 2.3$. The diffusion coefficient of citric acid determined using the RDA is 24% lower than that given by Levien (1955). This is probably due to following reasons: (1) calcium citrate precipitation on the disk surface, which acted as a diffusion barrier, (2) the diffusion coefficient of the citric acid was measured in solutions that contained more than 1,900 mg/l calcium ions. The calcium ions may act as counter ions, diffusing from the reaction boundary to the bulk solution (Conway et al., 1999), and hence decrease the diffusion coefficient of citric acid, and (3) the diffusion of the H^+ from the bulk solution to the disk was neglected. This may also affect the diffusion coefficient measured by the RDA.

Effect of temperature on the effective diffusion coefficient of citric acid

Figure 2 and **Table 1** show the effect of temperature on the effective diffusion coefficients of citric acid in its reaction solutions of initial concentration of 7.5 wt% at 1,000 psi. The temperature dependence of diffusion coefficients is usually quantified using the Arrhenius equation:

$$D = D_0 \exp\left(\frac{-E_a}{RT}\right) \quad (6)$$

where D_0 is the maximum diffusion coefficient (at infinite temperature), E_a is the diffusion activation energy (J/mol), R is the universal gas constant (8.314 J/mol/K), and T is temperature (K).

From **Figure 2**, it is evident that the effect of temperature on the effective diffusion coefficient of citric acid follows Arrhenius law. The activation energy was found to be 37.9 kJ/mol .

Conclusions

1. The dissolution rate was found to be dependent on reaction temperature, and the disk rotational speed.
2. The presence of counter calcium ions and the calcium citrate precipitation had significant effect on the effective diffusion coefficient of citric acid.
3. The effect of temperature on the effective diffusion coefficient of citric acid was found to follow Arrhenius law.

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Table 1: Effect of temperature on the diffusion coefficient of citric acid at initial acid concentration of 7.5 wt% and 1,000 psi.

D, cm²/s	ln (D)	T, K	1/T, K⁻¹
1.3634E -6	-13.505	298	0.003356
2.68E -6	-12.830	313	0.003195
4.5E -6	-12.311	323	0.003096

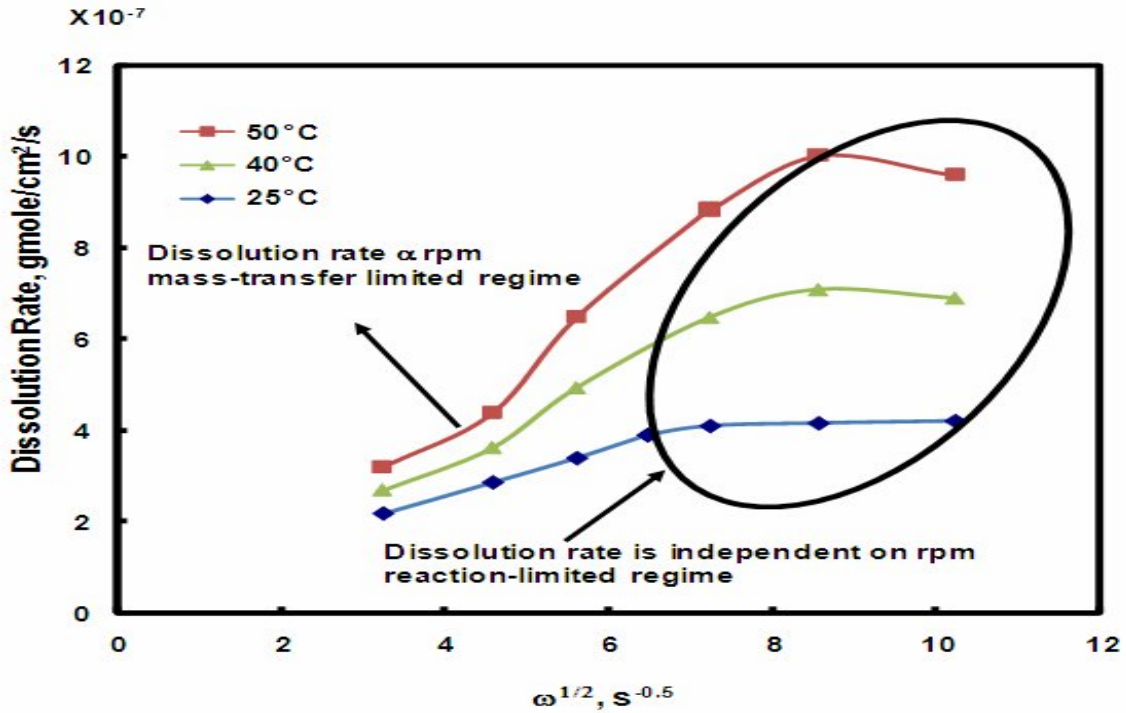


Figure 1: Dissolution rate of calcite in citric acid solutions of initial concentration of 7.5 wt% as a function of reaction temperature at rotational speeds of 100 to 1,000 rpm and 1,000 psi.

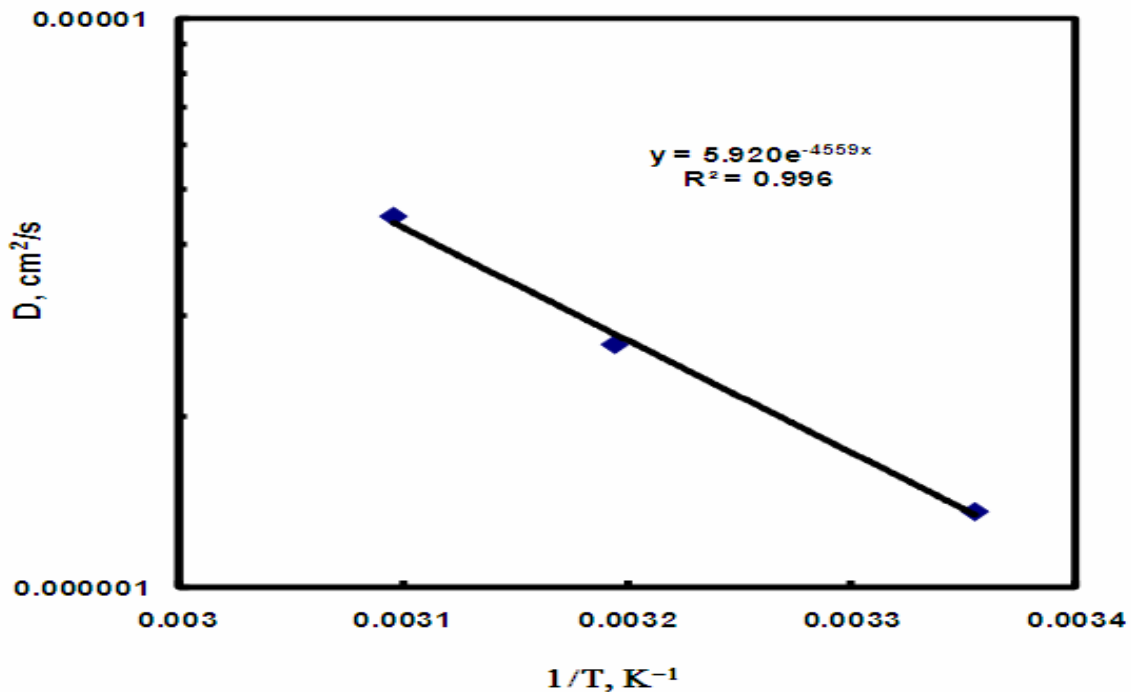


Figure 2: Diffusion coefficient of 7.5 wt% citric acid as a function of temperature at 1,000 psi.