

REACTION RATE OF METHANESULFONIC ACID (MSA) SOLUTIONS WITH  
CALCITE USING A ROTATING DISK APPARATUS

A Thesis

by

SAJJAAT MUHEMMED REYATH

Submitted to the Office of Graduate and Professional Studies of  
Texas A&M University  
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Chair of Committee, Hisham A. Nasr-El-Din  
Committee Members, Mahmoud El-Halwagi  
Zoya Heidari

Head of Department, A. Daniel Hill

December 2015

Major Subject: Petroleum Engineering

Copyright 2015 Sajjaat Muhemmed Reyath

## ABSTRACT

Methanesulfonic acid (MSA) has been proven as a scale remover and, more recently, as a stand-alone stimulation fluid in carbonate acidizing. MSA is a strong alkyl sulfonic acid having a pK value of -1.9, and it dissolves carbonate and oxides with its calcium water-soluble salts. Although the acid has many promising results for acidizing, little is known in relation to its detailed kinetics. This study aims to understand the reaction profile of MSA to provide relevant information to scientists and engineers to design acidizing jobs with this improved fluid.

The dissolution of calcite in MSA was studied with the aid of a rotating disk system at 1000 psig in the temperature range 73-250°F. As a result of this study, dissolution rate parameters for this system were reported for the first time. Details of the approach for this study include using marble disks of 1.5-in. diameter and 0.7-in. thickness. The dissolution rate was found by measuring the calcium concentration in the effluent as a function of time using inductively coupled plasma optical emission spectrometry (ICP-OES). The effects of MSA concentrations (5 to 20 wt%), disk rotational speeds (100 to 1500 rpm), and temperature on the rate of dissolution were also investigated.

Experimental results showed that, within the range of temperatures tested, the dissolution rate of MSA with calcite was mass-transfer limited, even at high disk rotation speeds and at high temperatures. At 5 wt% MSA concentration and at room temperature (73°F), the

rate of reaction was controlled by both mass transfer and surface reaction regime. The diffusion coefficient of a 5 wt% MSA fluid at 150°F was found to be  $3.00 \times 10^{-4} \text{ cm}^2/\text{s}$ , and at 250°F the diffusion coefficient was found to be  $9.76 \times 10^{-4} \text{ cm}^2/\text{s}$ . The acid diffusivity increased with increasing system temperature. At 5 wt% MSA, the effect of diffusion on temperature followed the Arrhenius law and the activation energy and the pre-exponential constant for diffusion were found to be 30 KJ/mole K and  $9.485 \text{ cm}^2/\text{s}$ , respectively.

Determination of the dissolution rate of MSA will increase the understanding of its performance as a stand-alone stimulation fluid. Its high acidity, high solubility of its calcium salts, and good thermal stability, along with its low corrosivity and readily biodegradable composition, makes this acid an attractive alternative to HCl in designing high-temperature acidizing applications.

## ACKNOWLEDGEMENTS

I would like to thank my committee chair, Dr. Nasr-El-Din, for his guidance and for providing me with the opportunity to further my education and learning. I would also like to thank Dr. Heidari and Dr. El-Halwagi for serving on my committee. My friends and colleagues also deserve thanks for their constant encouragement during the course of my research and for making my time at Texas A&M University an enjoyable one. Finally, I would like to thank my parents for their constant support and faith in me.

## NOMENCLATURE

$A_0$	Initial surface area of the disk, $\text{cm}^2$
$C_b$	Concentration of MSA in the bulk solution, $\text{gmol}/\text{cm}^3$
$C_s$	Concentration of MSA at the surface, $\text{gmol}/\text{cm}^3$
$D$	Diffusion coefficient, $\text{cm}^2/\text{s}$
$D_0$	Pre-exponential constant, $\text{cm}^2/\text{s}$
$E_a$	Diffusion activation energy, $\text{KJ}/\text{mole}$
$K_m$	Mass transfer coefficient, $\text{cm}/\text{s}$
$N_{ca}$	Moles of calcium in the solution, moles
$R$	Universal gas constant = $8.314 \text{ J}/(\text{mole} \cdot ^\circ\text{K})$
$R_{MT}$	Rate of mass transfer, $\text{gmol}/\text{cm}^2 \cdot \text{s}$
$Sc$	Schmidt number ( $\nu/D$ )
$t$	Time, s
$T$	Absolute temperature, $^\circ\text{K}$
$\omega$	Disk rotational speed, $\text{s}^{-1}$
$\rho$	Fluid density, $\text{g}/\text{cm}^3$
$\mu$	Fluid viscosity, $\text{g}/\text{cm} \cdot \text{s}$
$\nu$	Kinematic viscosity, $\text{cm}^2/\text{s}$

## TABLE OF CONTENTS

	Page
ABSTRACT .....	ii
ACKNOWLEDGEMENTS .....	iv
NOMENCLATURE .....	v
TABLE OF CONTENTS .....	vi
LIST OF FIGURES .....	viii
LIST OF TABLES .....	x
CHAPTER I INTRODUCTION AND LITERATURE REVIEW .....	1
Carbonate Acidizing .....	2
Motivation for Thesis .....	4
Methanesulfonic Acid (MSA) .....	8
High Acid Strength .....	9
Solubility of Reaction Products .....	10
Vapor Pressure .....	11
Corrosion Behavior of MSA .....	12
Objective of Research .....	13
CHAPTER II ROTATING DISK MODEL .....	14
CHAPTER III MATERIALS AND EQUIPMENT .....	17
Porosity .....	17
Composition .....	18
Acid Preparation .....	18
Fluid Properties .....	19
Density .....	19
Viscosity .....	21
CHAPTER IV REACTION OF MSA WITH CALCITE .....	23
Rotating Disk Apparatus .....	24

CHAPTER V DISSOLUTION RATE AND MASS TRANSPORT STUDY .....	26
CHAPTER VI DIFFUSION COEFFICIENT OF MSA AND THE EFFECT OF TEMPERATURE.....	34
CHAPTER VII APPLICATION AND CONCLUSIONS .....	37
CHAPTER VIII FUTUREWORK .....	39
REFERENCES .....	40
APPENDIX .....	44

## LIST OF FIGURES

	Page
Fig. 1.1— Wormholes in Matrix Acidizing .....	3
Fig. 1.2— Different dissolution patterns .....	6
Fig. 1.3— Dissolution patterns created by MSA in carbonate rock.....	8
Fig. 1.4— Manufacturing process of MSA.....	9
Fig. 1.5— Equilibrium constants of selected acids .....	10
Fig. 1.6— Concentration of saturated solutions of metal salts in g/l at 22°C.....	11
Fig. 1.7— Vapor pressure curves of selected acids .....	12
Fig. 3.3—Density meter .....	20
Fig. 3.4— Kinematic Viscosity of MSA solutions as a function of temperature .....	22
Fig. 4.1—Schematic diagram of the rotating disk apparatus .....	25
Fig. 5.1—Calcium concentration measured from ICP as a function of time .....	26
Fig. 5.2— Effect of disk rotational speed on the dissolution rate of 5 wt% MSA at 73°F.....	28
Fig. 5.3— Effect of temperature on the dissolution rate of 5 wt % MSA with calcite ....	29
Fig. 5.4— Effect of disk rotational speed on the dissolution rate of 10 wt% MSA at 73°F.....	29
Fig. 5.5— Effect of disk rotational speed on the dissolution rate of 20 wt% MSA at 73°F .....	30
Fig. 5.6— Effect of temperature on the dissolution rate of 10 wt % MSA with calcite .....	31
Fig. 5.7— Effect of temperature on the dissolution rate of 20 wt % MSA with calcite .....	31
Fig 5.8— Rate of dissolution as a function of bulk concentration at 1,500 rpm .....	32

Fig. 5.9— Sample tubes after 10 wt% MSA-calcite reaction at 73°F .....	33
Fig. 5.10— Sample tubes after 20 wt% MSA-calcite reaction at 73°F .....	33
Fig. 6.1—Diffusion coefficient of 5 wt% MSA as a function of inverse of temperature .....	36

## LIST OF TABLES

	Page
Table 1.1— pKa values for different acids .....	7
Table 3.1—Density of MSA solutions with the corrosion inhibitor .....	20
Table 3.2—Viscosity of MSA solutions with the corrosion inhibitor .....	22
Table 6.1—Diffusion coefficients of MSA at different concentrations .....	35

## CHAPTER I

### INTRODUCTION AND LITERATURE REVIEW

Acidizing is one of the oldest and most common technique used in the oil and gas industry to enhance hydrocarbon production. The use of successful acidizing treatments dates back to 1895 when Herman Frasch, chief chemist at Standard Oil company's refinery, Ohio proposed the idea of removing formation damage using muriatic acid also known as hydrochloric acid (HCl)(Williams 1979). Since the use of first successful acidizing treatment in 1895, this technique did not gain much attention until 1932 when Pure oil and Dow Chemical Company jointly stimulated the wells by pumping 500 gallons of HCl with an arsenic acid inhibitor. After the treatment, the well which was dead earlier produced 16 barrels/day.

Acidizing of petroleum reservoirs involves the injection of reactive fluid into the formation to dissolve the rock/materials causing formation damage in the near wellbore region. The dissolution of minerals increases the reservoir permeability in the near well bore region ensuring the flow of oil and gas. In the sandstone reservoir, a mixture of hydrochloric acid (HCl) and hydrofluoric acid (HF) commonly known as mud acid are injected into the reservoir to remove the damage. HCl dissolves carbonate minerals like calcite, dolomite and HF dissolves siliceous minerals like sodium feldspar and potassium feldspar. The quartz matrix remains relatively inert and intact. The reaction front and permeability front move uniformly through the porous medium as the reaction is limited

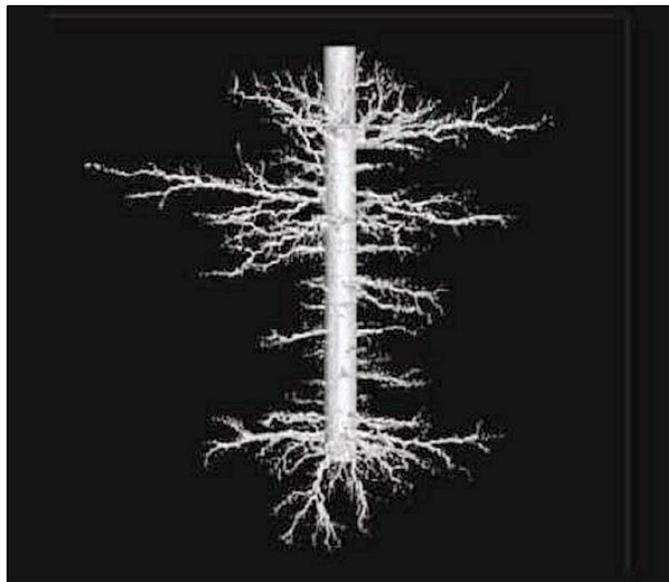
by the kinetics of surface reactions (Fogler, Lund, and McCune 1976, Lund and Fogler 1976, Fogler, Lund, and McCune 1975).

### **Carbonate Acidizing**

Carbonate acidizing can be broadly classified into acid fracturing and matrix acidizing. In acid fracturing, reactive acid is pumped into the reservoir at pressures sufficient to fracture the formation or open existing fractures. The reactive acid increases the fracture conductivity by etching the fractures unevenly that prop open the fractures even when pressures are relieved. Acid fracturing are not used in sandstone reservoirs as the inert matrix of the rock does not create sufficient etching which results in low fracture conductivity.

Matrix acidizing involves injecting reactive acid into the formation below fracture pressure creating conductive channels (wormholes) through the damage connecting wellbore and the reservoir (Guin, Schechter, and Silberberg 1971, Hoefner and Fogler 1988, Nierode and Williams 1971). These wormholes which are typically few feet in length, are formed in carbonate lithology because the acid is able to dissolve the rock matrix completely. Matrix treatments are desirable when there is a natural boundary like shale rock, water aquifer and fracturing the reservoir can lead adverse aftereffects. The carbonate rock basically consists of limestone and dolomite minerals and rate of dissolution of carbonate rock with HCl depends on the mineralogical composition of the rock. The dissolution of limestone by HCl is limited by the mass transfer at temperatures above 0°C (Lund et al. 1975) and the dissolution of dolomite by HCl is limited by the

surface reaction at temperatures below 40°C (Lund, Fogler, and McCune 1973). The most widely used mineral acid for acidizing is HCl. The concept of mass transfer and surface reaction limiting regimes will be discussed in the later chapters. The heterogeneity in the porous media and the influence of mass transfer results in the non-uniform dissolution of carbonates. The propagation of wormhole depends significantly on the flowrate and the properties of the fluid rock system. A good understanding of the dissolution pattern is necessary to design an effective stimulation system and the structure of the wormhole depends on the reaction rate and diffusion coefficient. This study is related to the dissolution of carbonate petroleum rock.



**Fig. 1.1—Wormholes in Matrix Acidizing.**

Hoefner and Fogler (1988) found that the structure of dissolution channels depends on the acid flowrate and fluid/rock properties and is governed by the Damkohler number for flow and reaction. It is defined as the ratio of the net rate of dissolution by acid to the rate

of convective transport of acid. For mass transfer limited reaction, the Damkohler number is given by

$$Da_{mt} = aD_e^{2/3}l/Q$$

Where  $D_e$  is the effective diffusion coefficient,  $Q$  is the flow rate,  $l$  is the pore length, and 'a' is a constant that depends on the carbonate sample. Damkohler number is useful in modelling the wormhole propagation in the reservoir. Furthermore when the dissolution is limited by the surface kinetics, then Damkohler number is given by

$$Da_{rxn} = ak_r dl/Q$$

Where  $k_r$  is the surface reaction rate constant and  $d$  is the pore diameter.

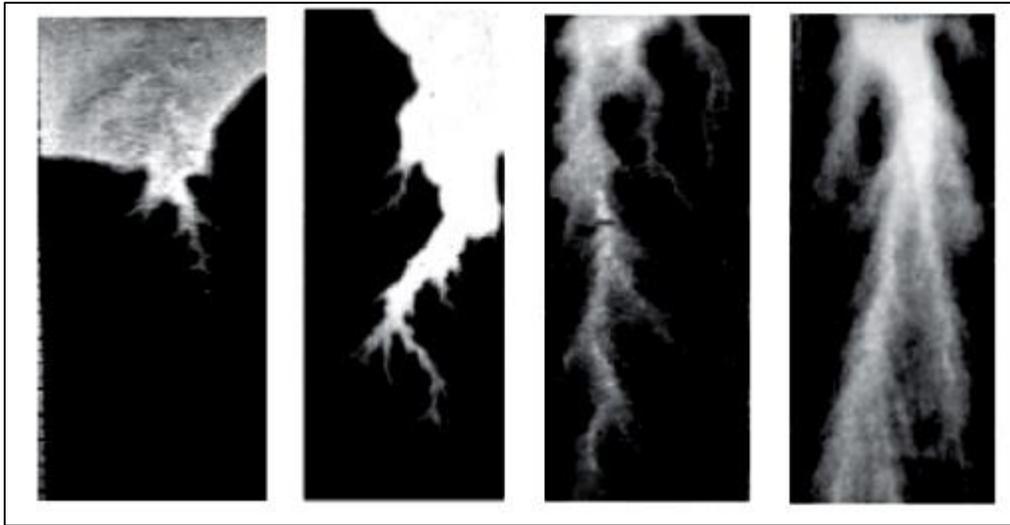
### **Motivation for Thesis**

HCl is the common mineral acid used in the industry for carbonate acidizing. It is easily available, economical and highly reactive towards carbonate rocks. Furthermore, the reaction products are soluble in water which makes HCl a perfect candidate for acidizing of petroleum reservoirs. However, using HCl also comes with many disadvantages. Its high reactivity causes severe corrosion problems to downhole equipment and the problem increases exponentially at elevated downhole temperatures and acid concentration. Barmatov et al. (2012) stated that corrosion rate of reactive acids towards stainless steel can be as high as 100 mm/year and the total annual cost of corrosion in oil and gas industry is estimated to be \$1.372 billion (Rajeev, Surendranathan, and Murthy 2012). The presence of ferric ions caused by corrosion leads to the formation of oil sludge which plugs the pores hence causing production issues. So corrosion inhibitors

are added to prevent the corrosion related issues. However, using corrosion inhibitors increases the total cost of acidizing jobs.

Environmentally, HCl has acute toxic effects. Due to its low vapor pressure, HCl fumes even at room temperatures which causes problems in handling and transportation of the acid. When HCl comes in contact with soil, the acid carries itself in the soil without decomposing causing damage to the ground water.

The high reactivity of HCl can also has disadvantages. In the shallow/tight formations, HCl causes a phenomenon known as face dissolution where the acid does not penetrate into the formation deep enough to cause wormhole formation but rather dissolves the complete face of the formation significantly. For these reasons, organic acids are used in the industry for the acidizing jobs. Organic acids such as acetic and formic acid are weak acids that have low  $H^+$  concentrations. However, since organic acids are weak, more quantity of acid is required to create good acidizing results and the problem of corrosion are still prevalent with the use of organic acids.



**Fig. 1.2—Different dissolution patterns (From left- Face dissolution, conical wormhole, dominant wormhole, ramified wormhole).**

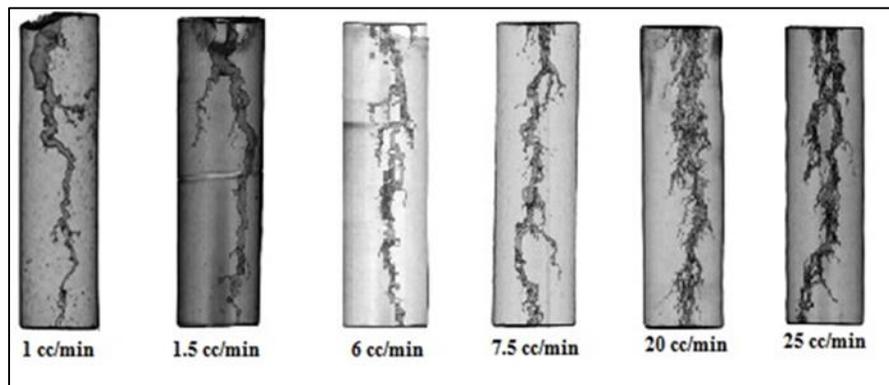
Chang et al. (2008) stated that organic acids cannot be used at high concentrations because of their limited solubility with calcium salts. Also, organic acids have low a dissociation constant and the degree of hydrogen ion generation decreases with increasing temperature. All the above mentioned disadvantages associated with strong mineral and weak organic acids in acidizing the damaged formation necessitated a less corrosive and environmental friendly strong acid. Sulfonic acids, which are classified as strong acids containing one or more sulfonic groups (- SO<sub>3</sub>H) having similar acidity characteristics to sulfuric acid, less corrosive and easily biodegradable have been recently proposed as an appropriate fit for high-temperature acidizing applications. The physical properties of sulfonic acids depend greatly on the nature of R-group, which usually consists of alkane, alkene, alkyne, and arene. Use of alkanesulfonic acids, particularly methanesulfonic acid (MSA) for acidizing applications was first proposed by Heidenfelder et al. (2009). MSA is a strong acid with a pK<sub>a</sub> value of -1.92 (Covington and Thompson 1974). In Table 1, a comparison of MSA

with other acids shows that MSA is a strong acid compared to other conventional acids used in the oil industry.

<u>Name of the Acid</u>	<u>pK<sub>a</sub></u>
Hydrochloric acid	-7.00
Sulfuric acid	-2.80
<b>Methanesulfonic acid</b>	-1.92
Formic acid	3.75
Citric acid	3.13
Hydrofluoric acid	4.00
Acetic acid	4.77

Table 1.1— pK<sub>a</sub> values for different acids from Guthrie (1978) and Fuller (2010).

MSA is generally considered to be a ‘green acid’ due to its environmental benefits (Gernon 1999). Finsgar and Milosev (2010) studied the corrosion behavior of 70 wt% aqueous MSA on different grades of steel and found steel to be resistant against localized and uniform corrosion with the maximum corrosion rate of 1 mm/year. Ortega et al. (2014) conducted a coreflood study in which it was found that MSA was effective in creating wormholes in limestone cores at different injection rates and at high temperature (250°F).



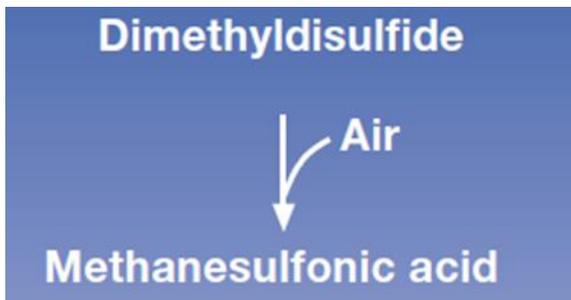
**Fig. 1.3—Dissolution patterns created by MSA in carbonate rocks.**

The figure above shows the dissolution patterns after injection of 10 wt% MSA at different injection rates at 250°F.

### **Methanesulfonic Acid (MSA)**

Methanesulfonic acid (MSA) is the simplest acid in the family of sulfonic acids. Sulfonic acids is a class of organic acid that has sulfur with formula  $\text{RSO}_3\text{H}$ , where R is generally alkanes, alkenes functional organic group. MSA has been used as a commercial electrolyte successfully for the past 20 years and now recently it has been proposed as a standalone acidizing fluid. MSA is a strong organic acid that can dissolve carbonate rocks without leaving behind any precipitates. It has many physical and chemical properties that makes MSA a suitable acid for acidizing carbonate rocks. MSA is also considered relatively less toxic and has many ecological advantages that will be discussed later in the chapter individually. MSA is manufactured commercially by the oxidation of

dimethyldisulfide (DMDS). It is also produced naturally by the same process which makes it part of natural Sulphur cycle(Baker, Kelly, and Murrell 1991).



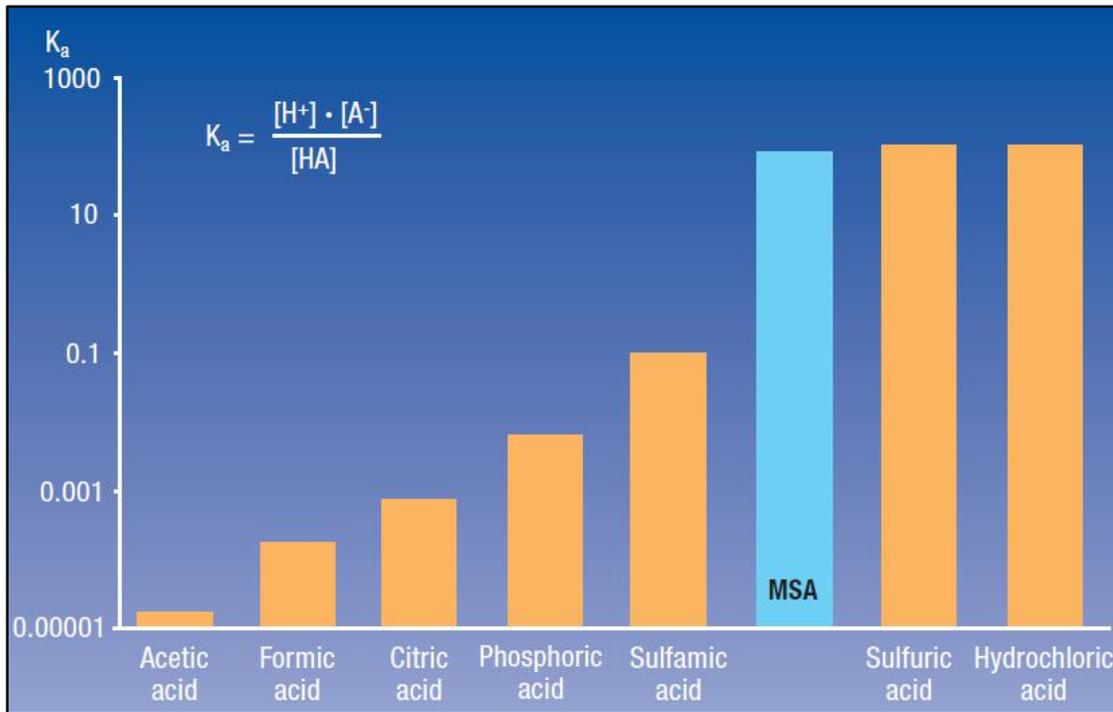
**Fig. 1.4—Manufacturing process of MSA.**

### High Acid Strength

The strength of an acid is defined as the ability of the acid to donate  $H^+$  ions. More availability of  $H^+$  ions make the acid the acid stronger acid. This is evaluated by the law of chemical equilibrium which states that the ratio of rate of forward reaction to the backward reaction is constant which in this case known as equilibrium constant ( $K_a$ ).

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

Where the species in the square brackets are the concentrations. By using the law of equilibrium, the concentration of  $H^+$  ions can be calculated. Below is the graph which shows the proton donation capacity of MSA.



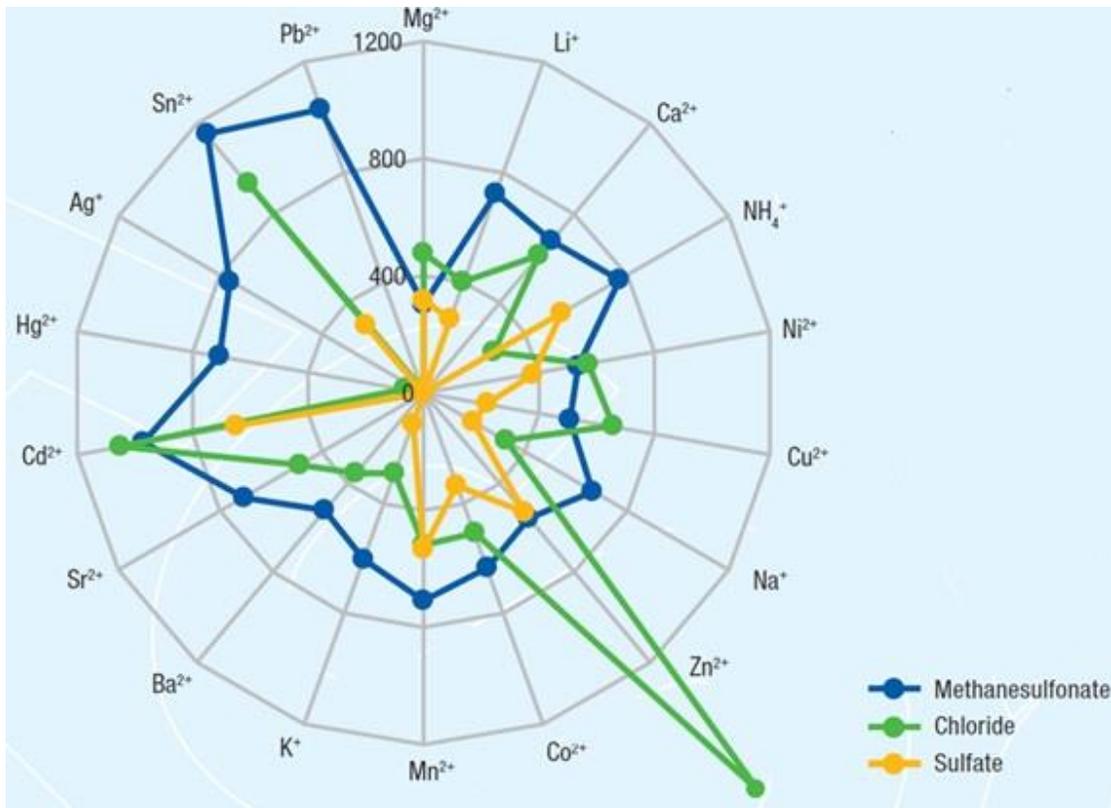
**Fig. 1.5—Equilibrium constants of selected acids (Data provided by BASF).**

It can be inferred from the above picture that MSA has the highest proton donor capacity in comparison to all organic acids. In other words, less quantity of acid is required to dissolve carbonate rock in comparison to other organic acids like acetic acid, citric acid and formic acid.

#### Solubility of Reaction Products

Although sulfuric acid is a strong acid, it cannot be employed in the acidizing as the reaction product calcium sulfate is not soluble in water. This precipitation of insoluble salts further damages the formation rock. So for good acidizing results, soluble reaction products are of significant importance. The reaction products of MSA have high solubility.

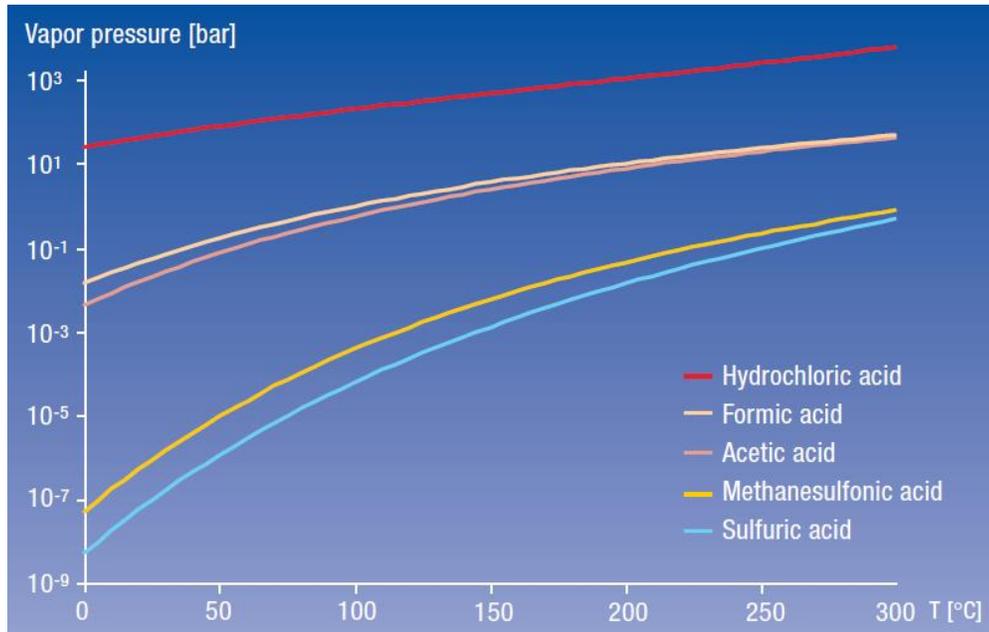
Below is the figure which shows the solubility of salts of MSA. Calcium has a solubility of 672 g/l in MSA at 22°C as compared to 611 g/l in Chloride.



**Fig. 1.6— Concentration of saturated solutions of metal salts in g/l at 22°C.**

### Vapor Pressure

Vapor pressure is defined as the pressure exerted by the liquid due to evaporation in a closed container. MSA has low vapor pressure making it odor-free acid without any toxic fumes unlike hydrochloric acid which gives out toxic fumes making it difficult to transport.



**Fig. 1.7—Vapor pressure curves of selected acids.**

#### Corrosion Behavior of MSA

Finšgar and Milošev (2010) investigated the corrosion rate of 70 wt% MSA with 304, 316 and 316Ti stainless steel grades. It was found that MSA has a maximum corrosion rate of 1 mm/year and minimum of 0.01 mm/year. The maximum corrosion rate of MSA was attributed to the chloride impurities present in the MSA and not by the MSA itself. The corrosion rate of 2 wt % HCl at room temperature is near to 5000 mm/year. The significantly low corrosion rate can be a great contribution in protecting in the downhole equipment where millions of dollars are spent each year to limit corrosion.

## **Objective of Research**

As discussed earlier, the laboratory coreflood studies showed the ability of MSA to create wormholes but there are some missing data in the literature regarding the dissolution of MSA with calcite. The aim of this study is to find:

1. The rate of dissolution of MSA with calcite.
2. The mass transport properties like diffusion coefficient and activation energy.

## CHAPTER II

### ROTATING DISK MODEL

For an acidizing treatment involving a solid rock and a fluid acid system, the reaction rate determination process is greatly affected by both the mass transport of the reactant fluids to the rock surface and the transport of products away from the surface. Therefore, the overall reaction comprises of three steps: (1) the transfer of the reactant from the bulk of solution to the surface of the solid, (2) the surface reaction, and (3) the transfer of the products from the surface into the bulk of the solution again. The overall reaction kinetics are controlled by the rate of the slowest step and are referred to as the rate-limiting or the controlling step. The effect of one step on the overall reaction can be accurately studied by eliminating the effects of all the other steps. For a reaction system, if the mass transport process is faster than the rate of surface reaction, then it is called surface reaction limited. On the other hand, if the diffusion to the surface is slower than the rate of surface reaction, then the process is called mass transfer limited. As per the studies conducted by Levich (1962) and Newmann (1966), the rate of mass transfer of a reactant to the solid surface in a laminar flow regime ( $Re < 3 \times 10^5$ ) is given by the following equation:

$$R_{MT} = k_m(C_b - C_s) \qquad \text{Eq. 2.1}$$

Where  $C_b$  and  $C_s$  represent the bulk and surface concentrations of the transferring species, respectively.  $K_m$  represents the mass transfer coefficient, which can be determined as follows:

$$k_m = \frac{0.60248(Sc^{-\frac{2}{3}})(\sqrt{v\omega})}{1+0.2980\left(Sc^{-\frac{1}{3}}\right)+0.1451(Sc^{-\frac{2}{3}})} \quad \text{Eq. 2.2}$$

$$Sc = \frac{v}{D} \quad \text{Eq. 2.3}$$

$$v = \frac{\mu}{\rho} \quad \text{Eq. 2.4}$$

For a mass transfer limited regime, where the rate of reactant consumption at the surface is lower than the rate of mass transport, it can be assumed that there is negligible concentration of the reactant at the solid surface. Hence, the second term of Eq. 2.1 can be neglected by substituting Eq. 2.2 into Eq. 2.1. The final form of the mass transfer rate for a laminar and Newtonian fluid can be written as follows:

$$R_{MT} = \frac{0.60248(Sc^{-\frac{2}{3}})(\sqrt{v})C_b}{1+0.2980\left(Sc^{-\frac{1}{3}}\right)+0.1451(Sc^{-\frac{2}{3}})} \omega^{1/2} \quad \text{Eq.2.5}$$

As per Eq. 2.5, it can be inferred that for the mass transfer limited regime, and the rate of mass transfer (and hence, the rate of dissolution) is linearly proportional with the square

root of the disk rotating speed. The effective diffusivity of MSA at 150 and 250°F can also be determined by using Eq. 2.5 as Schmidt number as a function of diffusivity and kinematic viscosity.

### CHAPTER III

#### MATERIALS AND EQUIPMENT

##### **Porosity**

The porosity is defined by the ratio of pore volume to the bulk volume in the porous media. It is usually represented in percentage. The most common method of determining porosity is to saturate the cores with deionized water. The water is injected into the small pores by placing the cores in a closed chamber which is half filled with deionized water and high pressure suction pump is used to create a vacuum in the chamber. This method enables water to push itself into the connected pores. The difference in dry weight of the core and saturated cores will be the weight of the water that is in the pores which is also known as pore volume and the ratio of pore volume and bulk volume will result in effective porosity. But this method of finding porosity is not possible for marble cores where the pores are very small. So, in order to measure porosity accurately, helium porosity meter is used.

Helium porosity meter works on the principle of Boyle's law, which states that, at constant temperature and for a fixed mass, the product of temperature and pressure of a gas is constant. So Helium porosity meter consist of cylindrical chamber in which metallic disks of size equivalent to the inner diameter of the chamber is placed and Helium gas is made passed through the metallic chamber and the average pressure reading is noted. Subsequently, the some of the metallic disks are replaced with marble core and the change

in pressure is noted down. The ratio of change in pore volume and the bulk volume will result in porosity of the disk.

### **Composition**

The mineralogy of the rock surface reacting with the acid can be estimated by performing an X-ray Fluorescence (XRF) analysis. In this technique, the disk surface is bombarded with high energy X-rays or gamma rays and the emission of characteristic secondary wavelets are analyzed to determine the composition of the solid rock surface. A cut-off value of 97% calcium oxide (CaO) was set to make sure that only high purity cores are chosen for the rotating disk apparatus experiments. Having a composition screen reduces the presence of impurities at the rock surface and therefore negates their impact on the reaction kinetics.

### **Acid Preparation**

The different acid concentrations (5, 10, and 20 wt%) was prepared using MSA. The initial concentration of acid was 100 wt%, which was diluted to the required concentrations using deionized water having a resistivity of 18.2 M $\Omega$ .cm at 25°C. 1 vol% of corrosion inhibitor was used for 5 and 10 wt% of acid concentration, and 3 vol% of corrosion inhibitor was used for 20 wt% acid concentration. An increased concentration of corrosion inhibitor for 20 wt% acid was used for the safety of the equipment as MSA is a highly reactive acid.

## **Fluid Properties**

Rheological properties of MSA solutions (0.5, 1.0, and 2.0 molar concentrations) at different temperature conditions were carried out by the following methods:

### Density

Density of a substance is defined as the ratio of its mass to its volume. The density of a fluid varies with change in temperature and therefore it is important to measure it accurately at all the different temperature conditions. At room temperature, density measurements were done using a pycnometer. A pycnometer is a simple glass flask whose dry weight and volume is known. A sample fluid is then used to fill the pycnometer completely and the gas bubbles (if any present) are expelled out. The incremental weight gain is then measured, which corresponds to the weight of the known volume of the sample and hence the fluid's density is estimated.

At higher temperature conditions, instead of pycnometer, a high temperature high pressure density meter was used. This equipment can determine the density of the fluid sample injected at different temperature conditions ranging from 32-200°F. Fig. 3.3 shows both these devices.



**Fig. 3.3—Density Meter.**

Temperature (°F)	Density (g/cm <sup>3</sup> )		
	5 wt% MSA	10 wt% MSA	20 wt% MSA
86	1.0193	1.0382	1.0910
104	1.0176	1.0351	1.0819
122	1.0140	1.0300	1.0771
140	1.0095	1.0142	1.0719
158	1.0065	0.9980	1.0650
176	1.0029	0.9972	1.0580
194	1.0016	0.9951	1.0420

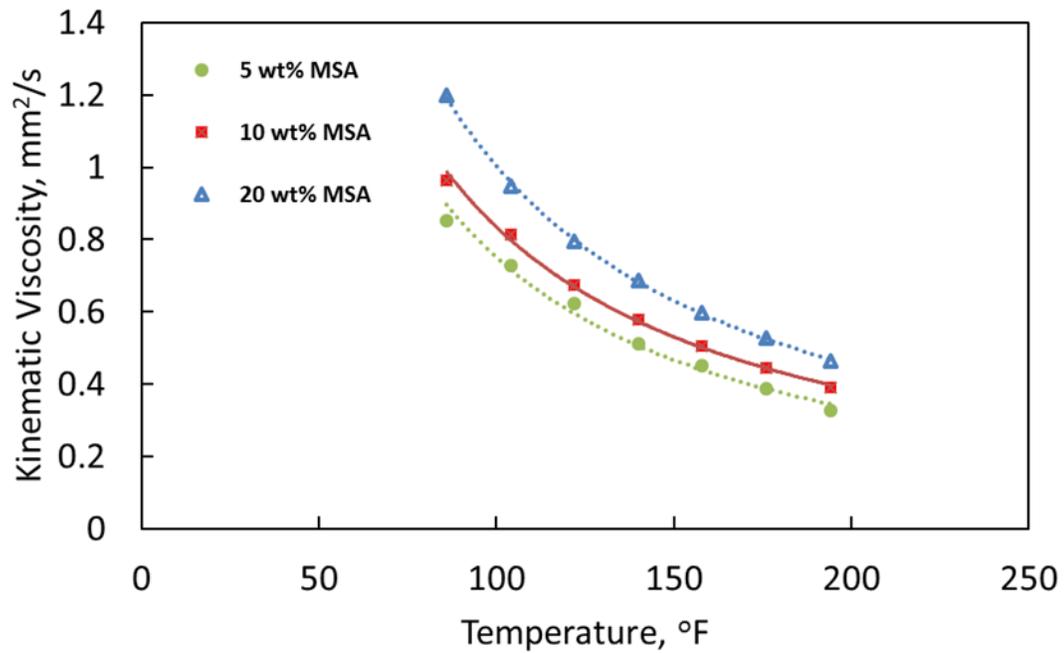
**Table 3.1—Density of MSA solutions with the corrosion inhibitor.**

## Viscosity

A fluid's resistance to flow is defined as its viscosity. Similar to density, fluid's viscosity also varies with temperature. Use of capillary viscometer is the simplest way to measure the viscosity of a Newtonian fluid. A capillary viscometer consists of three capillary tubes of different diameters. Small volume of sample (about 10 ml) is injected into the capillary and the entire system is then immersed in an oil bath. The temperature of the oil bath can be altered and the once the stabilized temperature condition is reached, the sample is raised through the biggest capillary tube by using a vacuum pump. The fluid is then allowed to drop down as per the gravitational force and the time taken by it to move from point 1 to point 2 is recorded. This time can then be multiplied by the capillary constant value to determine the kinematic viscosity of the sample. Dynamic viscosity was measured by multiplying the kinematic viscosity of the fluid with its density at the given temperature.

Temperature (°F)	Viscosity (mm <sup>2</sup> /s)		
	5 wt% MSA	10 wt% MSA	20 wt% MSA
86	1.005	1.113	1.200
104	0.825	0.863	0.948
122	0.585	0.675	0.795
140	0.473	0.579	0.687
158	0.449	0.504	0.597
176	0.421	0.444	0.528
194	0.402	0.431	0.465

**Table 3.2—Viscosity of MSA solutions with the corrosion inhibitor.**



**Fig. 3.4—Kinematic Viscosity of MSA solutions as a function of temperature.**

## CHAPTER IV

### REACTION OF MSA WITH CALCITE

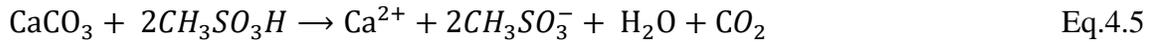
Calcite dissolution in different aqueous solutions has long been the interest of many researchers (Lund et al. 1975; Plummer et al. 1978; Pokrovsky et al. 2009). The surface reactions may be categorized into three different reactions based on the pH and partial pressure of carbon dioxide (Plummer et al. 1978). The reactions include: dissolution of calcite by hydrogen ion and calcite dissolution by carbonic acid and water, respectively.



When the partial pressure of  $\text{CO}_2$  is less than 0.1 atm, the concentration of  $\text{H}_2\text{CO}_3$  is negligible, and Eq. 4.1 represents the dominant reaction at low pH. A high pH (Eq. 4.2) is the dominant reaction. Since the reaction of MSA with calcite is carried out under a nitrogen atmosphere of pressure greater than 60 atm, Eq. 4.1 can be considered the dominant reaction. MSA is a relatively strong acid, and in aqueous phase, it supposed to exist in equilibrium with  $\text{CH}_3\text{SO}_2\text{O}^-$  and  $\text{H}_3\text{O}^+$ .

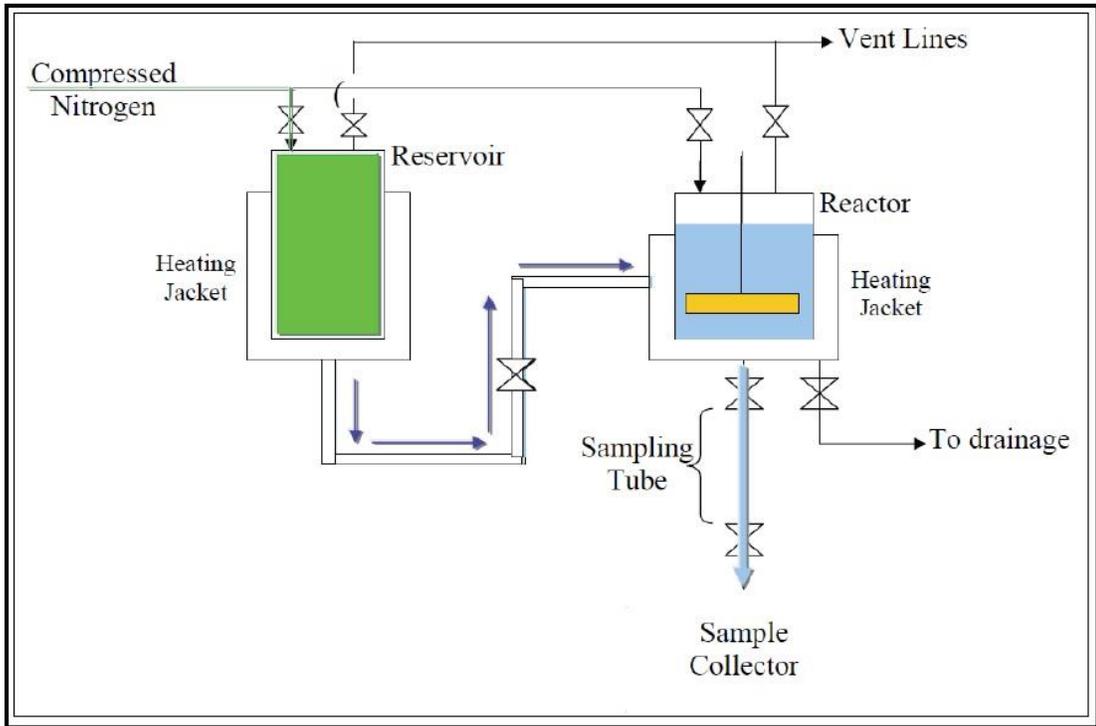


The main reaction of MSA with calcite can be written as follows:



### **Rotating Disk Apparatus**

The rate of dissolution was determined using the rotating disk apparatus, as shown in **Fig. 4.6**. After preparing the disks, the core sample was fixed in the holder assembly and coated with heat-shrinkable Teflon rollcover. It was done so that only the outer face of the disk was exposed where the reaction takes place. Then, the reservoir vessel was filled with the prepared acid and pressurized at 1,500 psig with nitrogen gas. Next, the core sample was mounted on a reactor vessel, and the experiment was conducted above 1,000 psig to keep CO<sub>2</sub> in the solution. This was done to prevent the CO<sub>2</sub> from affecting the hydrodynamics of the solution (Lund et al. 1973; Fredd and Fogler, 1998c). After setting the rotational speed of the disk to desired value, the timer was started at the moment when the acid was transferred from the reservoir vessel to the reactor vessel. Samples were taken every minute for a period of 10 minutes.

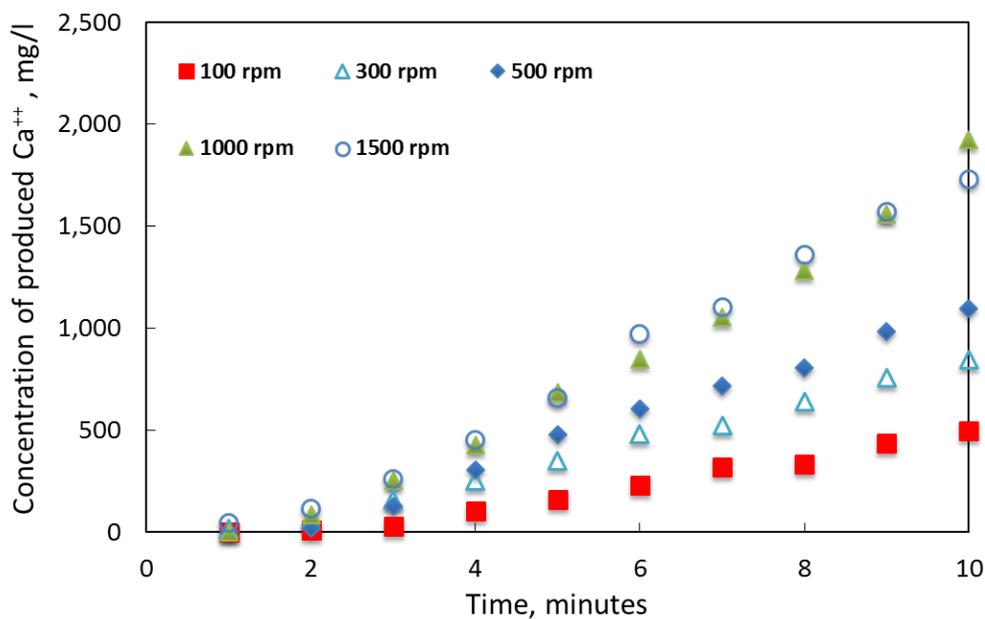


**Fig. 4.1—Schematic diagram of the rotating disk apparatus.**

## CHAPTER V

### DISSOLUTION RATE AND MASS TRANSPORT STUDY

Experiments were conducted on the rotating disk apparatus over three concentration profiles (5, 10, and 20 wt%) of MSA with different disk rotational speeds (100-1,500 rpm) and in a temperature range of 73-250°F. The amount of calcium consumed in the reaction was plotted against time to determine the rate of dissolution. **Fig. 5.1** shows typical plots of the moles of calcium ions [ $\text{Ca}^{2+}$ ] produced as a function of the total reaction time (10 mins) at different rotational speeds.



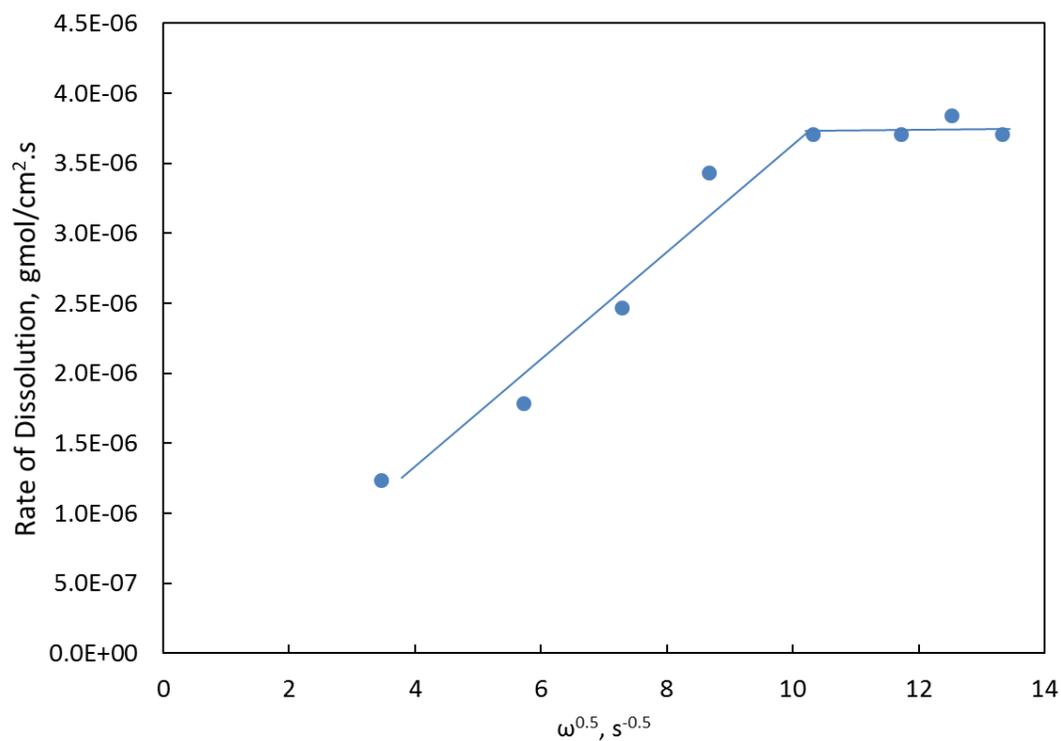
**Fig. 5.1**—Calcium concentration measured from ICP as a function of time.

These plots were used to determine the calcite dissolution rate. The dissolution rate of calcite was calculated from the slope of the plot containing moles of calcium in the solution with time which as follows:

$$\text{Calcite dissolution rate} = -\frac{dN_{Ca}}{A_0 dt}$$

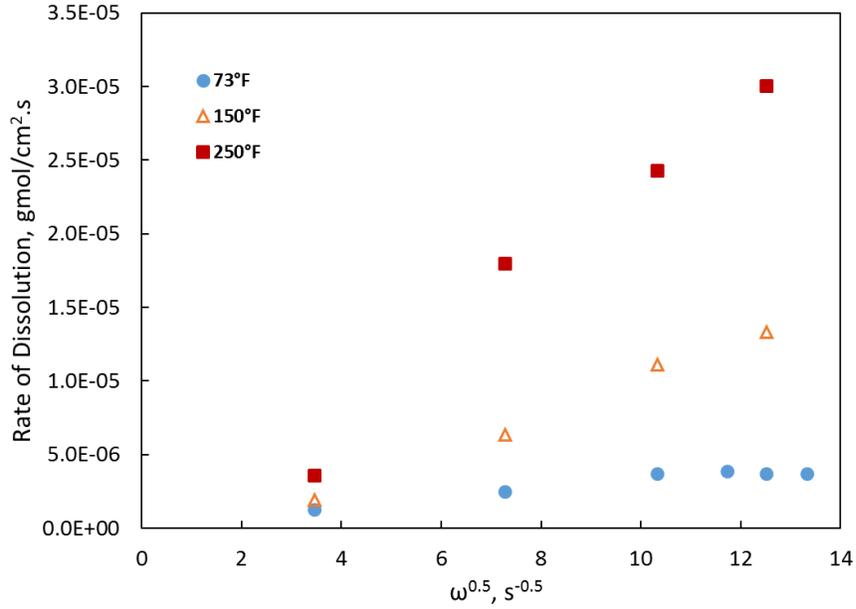
Where, the initial surface area of the disk  $A_0$ , and time  $t$ . Lund et al. (1974) stated that the mass transport of a rotating disk with an infinite surface reaction rate is proportional to the square root of the disk rotating speed. In other words, the rate of dissolution will increase with the increasing disk rotational speed. So the results obtained were used to determine whether the reaction of calcite with MSA was limited by surface reaction or mass transport regime.

The rate of calcite dissolution at 5 wt% MSA was calculated at rotational speeds in the range of 100-1,500 rpm at three different temperatures (73, 150, 250°F), as shown in **Fig. 5.3**. As per Eq. 5, and at 73°F, the rate of dissolution plotted against square root of disk rotational speed showed a straight line for the whole range of disk rotational speeds (100-1,000 rpm), indicating the dissolution rate was predominantly limited by the mass transfer of reacting species from bulk to the reaction surface. At higher disk rotational speeds (>1,000 rpm), the rate of dissolution became independent of disk rotational speed, indicating the rate of reaction was limited by surface reaction regime. This trend can be seen in **Fig. 5.2** where the curve became plateau from 1,000 rpm.

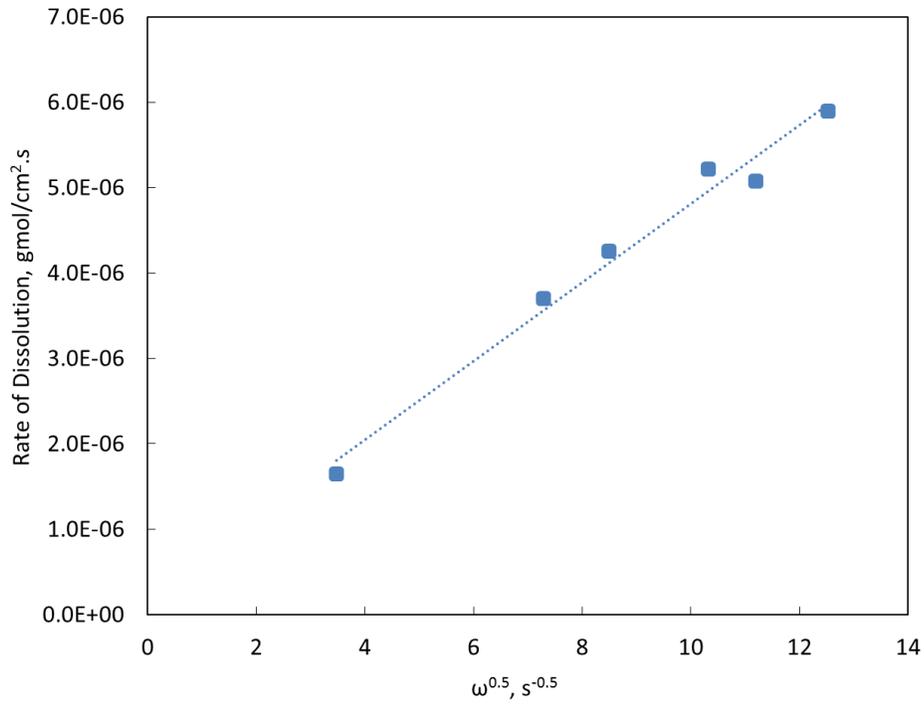


**Fig. 5.2— Effect of disk rotational speed on the dissolution rate of 5 wt% MSA at 73°F.**

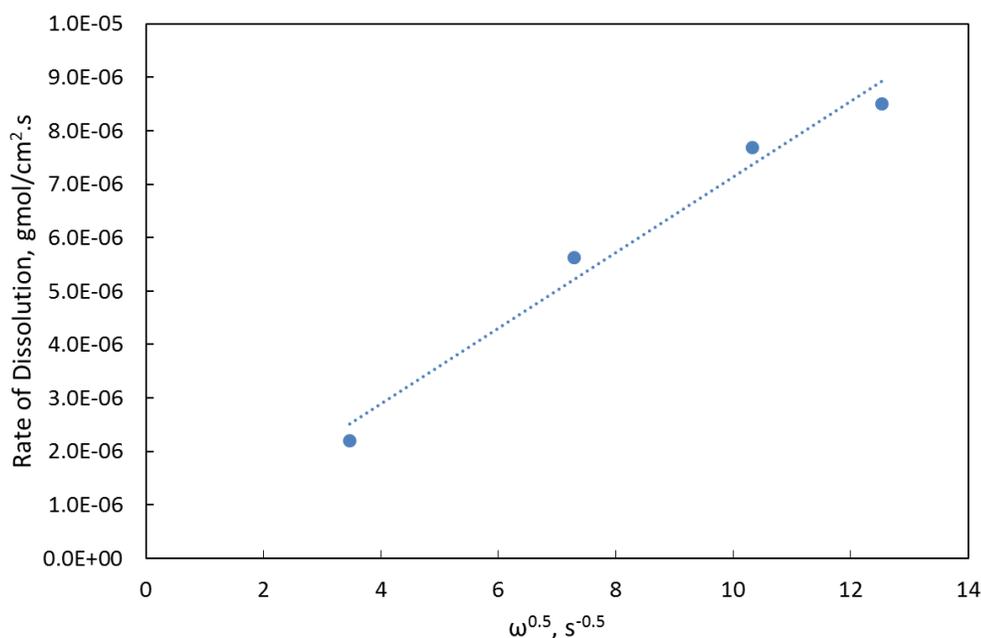
At elevated temperatures, dissolution rate became completely mass transfer limiting even at high disk rotational speeds (up to 1,500 rpm). A plot showing comparison of dissolution rate at different temperatures is shown in **Fig. 5.3**. As the temperature is increased, the rate of transport of reacting species ( $H^+$ ) from the bulk to the reaction surface is increased there by increasing the dissolution rate.



**Fig. 5.3— Effect of temperature on the dissolution rate of 5 wt % MSA with calcite.**



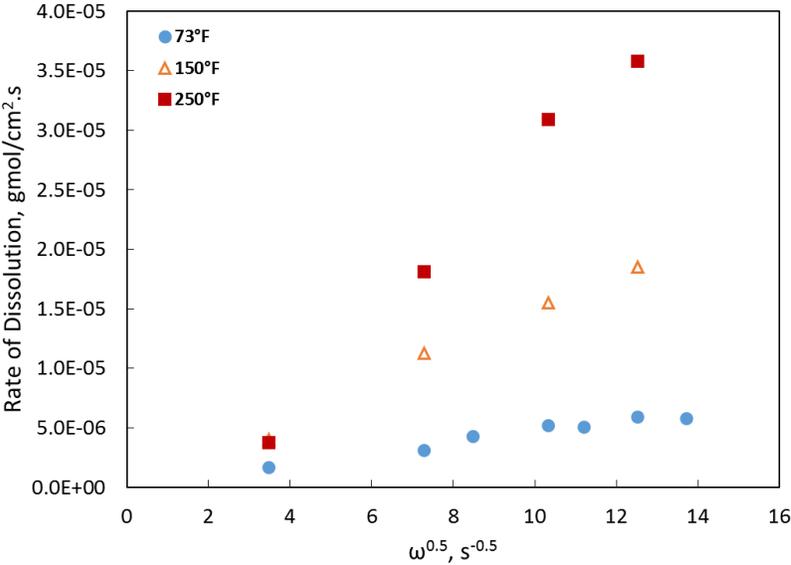
**Fig. 5.4— Effect of disk rotational speed on the dissolution rate of 10 wt% MSA at 73°F.**



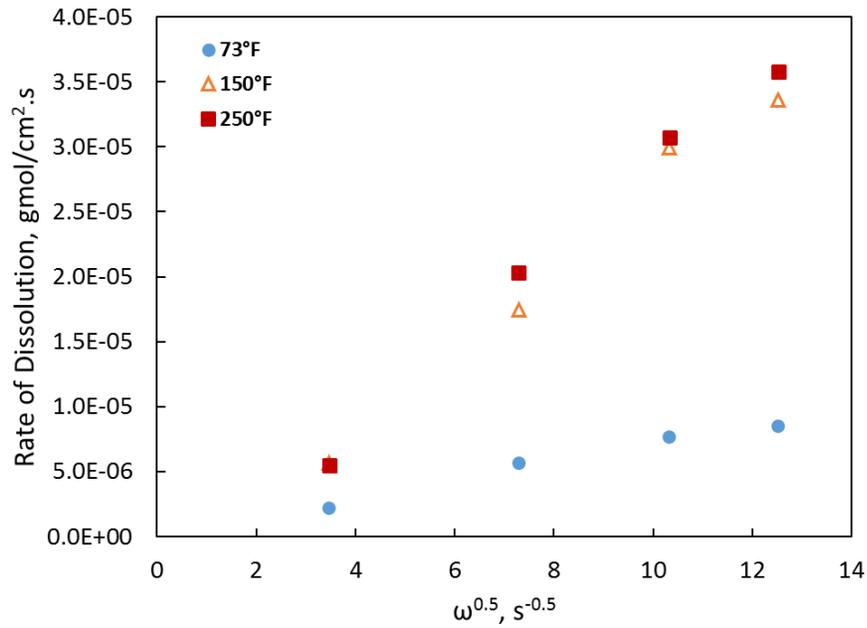
**Fig. 5.5— Effect of disk rotational speed on the dissolution rate of 20 wt% MSA at 73°F.**

The same procedure was followed to determine dissolution rate of 10 and 20 wt% MSA with calcite, which is shown in **Figs. 5.4 and 5.5**. It can be observed that, when initial concentration of acid is increased, the appearance of surface reaction regime is extended and the reaction is limited by mass transfer up to 1,500 rpm. This is because of the increased concentration of H<sup>+</sup> ions in the bulk. A comparison of dissolution rates at different temperatures is shown in **Figs. 5.6 and 5.7**. From Figs. 8 and 9, it was observed that the difference between average dissolution rates decreases with increase in temperature and concentration of MSA. The change in dissolution rate can be seen significantly at 150°F. From **Fig. 5.8**, it can be observed that at room temperature, the rate of dissolution and initial bulk concentration follows a linear relationship up to 20 wt% MSA and at 1,500 rpm. With the increase in temperature, the linear dependency between

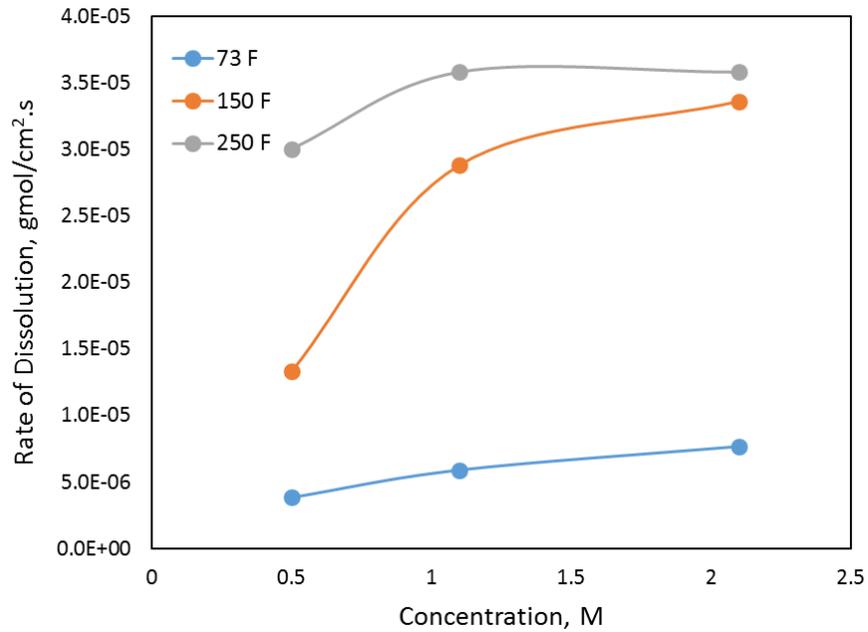
dissolution rate and initial bulk concentration decreases and at 250°F, the rate of dissolution becomes constant after 10 wt%. it can be concluded that the optimum initial concentration of MSA at 250°F for maximum dissolution of calcite is 10 wt%.



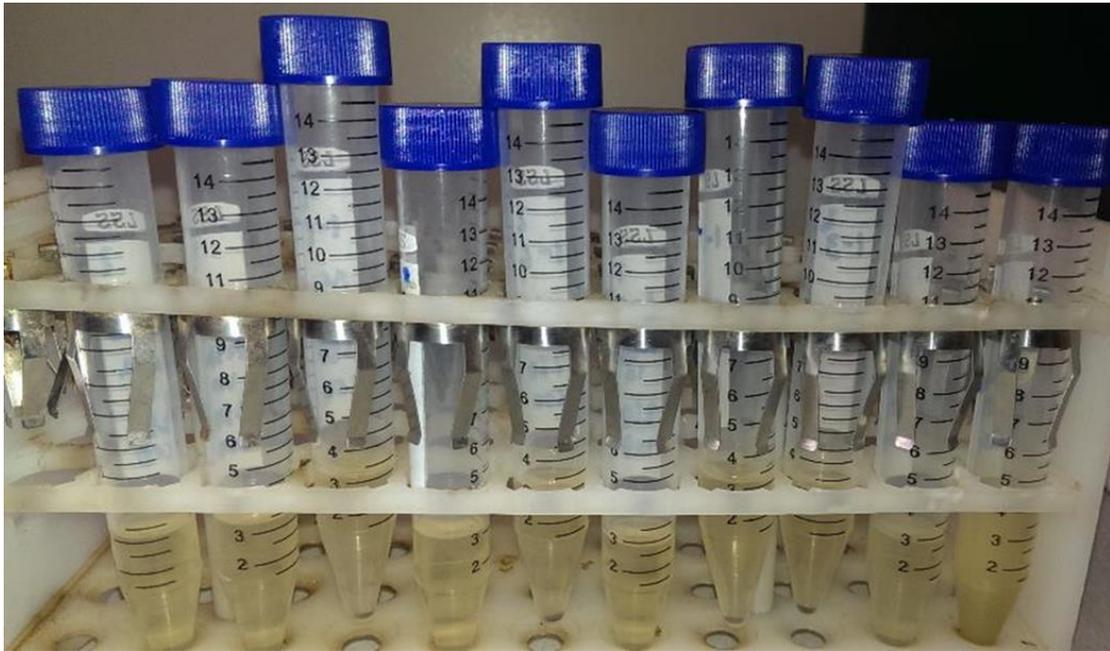
**Fig. 5.6— Effect of temperature on the dissolution rate of 10 wt % MSA with calcite.**



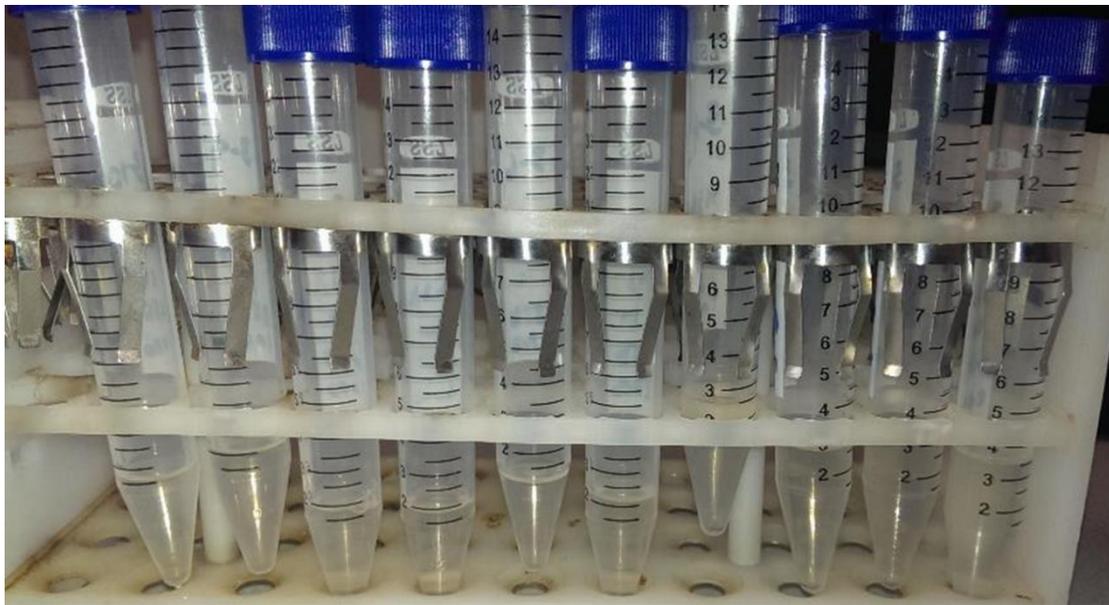
**Fig. 5.7— Effect of temperature on the dissolution rate of 20 wt % MSA with calcite.**



**Fig 5.8— Rate of dissolution as a function of bulk concentration at 1,500 rpm**



**Fig. 5.9— Sample tubes after 10 wt% MSA-calcite reaction at 73°F.**



**Fig. 5.10— Sample tubes after 20 wt% MSA-calcite reaction at 73°F.**

## CHAPTER VI

### DIFFUSION COEFFICIENT OF MSA AND THE EFFECT OF TEMPERATURE

As stated earlier, the transfer of reacting species from the bulk to the surface and the transfer of products from the surface to the bulk occurs due to a concentration gradient created between bulk and the surface. According to Eq. 2.2, a plot between rate of dissolution and the square root of disk rotational speed at the mass transfer limiting regime should yield a straight line, which means that rate dissolution is completely controlled by diffusion of the reacting species to the surface. This plot can be used to calculate the effective diffusivity of the reacting species to the surface and products back to bulk, which was found to be  $9.7 \times 10^{-6} \text{ cm}^2/\text{s}$  at 5 wt% MSA and 73°F. A similar approach was used to calculate diffusivity at 10 and 20 wt.% MSA and at different temperatures, which are shown in Table 2. **Fig. 6.1** shows the effect of temperature on diffusion coefficient of MSA at its initial concentration of 5 wt% at 1,000 psig. The dependence of the diffusion coefficient on temperature can be quantified using the Arrhenius equation:

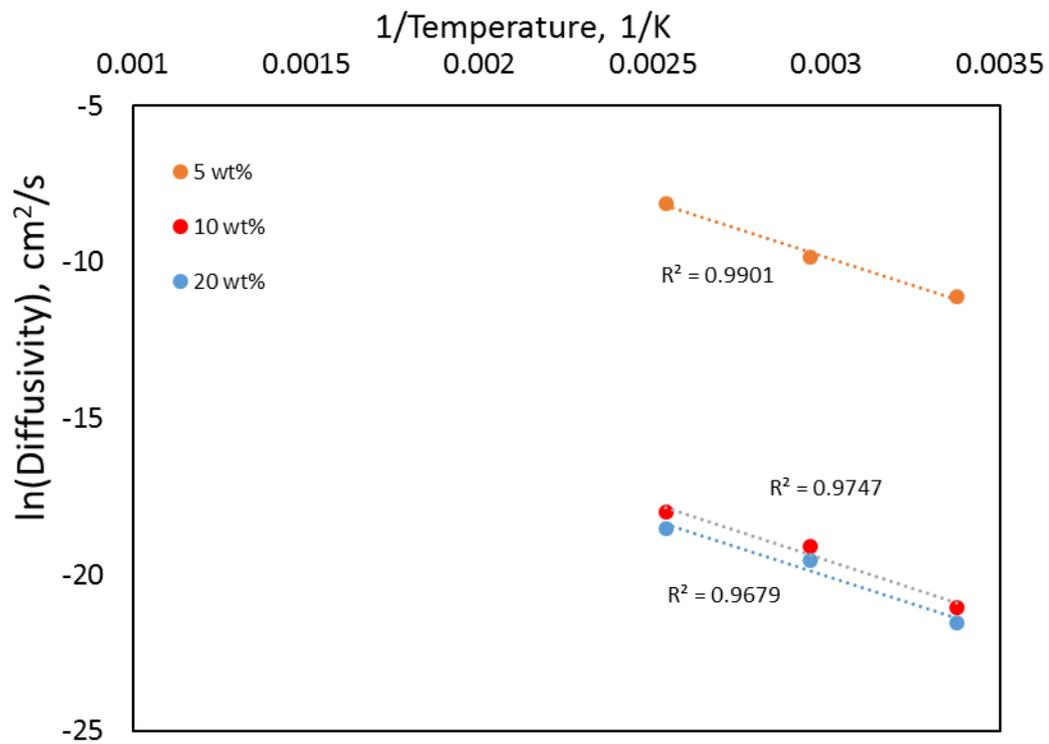
$$D = D_0 \exp\left(\frac{-E_a}{RT}\right)$$

As expected, the diffusion coefficient increased with an increase in temperature, and its activation energy at the mass transfer regime was found to be 30.1 KJ/mole with the pre-exponential constant as  $5.6 \times 10^{-4} \text{ cm}^2/\text{s}$ . To draw a comparison, the activation energy for calcite dissolution rate from mass transfer limited regime was reported as 19 KJ/mole for

HCl (Alkattan et al. 1998) and 14 KJ/mole (Barton and Vatanatham 1976) for H<sub>2</sub>SO<sub>4</sub>, respectively.

Temperature (°F)	Diffusion coefficient (cm <sup>2</sup> /s)		
	5 wt% MSA	10 wt% MSA	20 wt% MSA
73	4.40 x 10 <sup>-5</sup>	1.73 x 10 <sup>-5</sup>	7.60 x 10 <sup>-6</sup>
150	3.00 x 10 <sup>-4</sup>	2.91x 10 <sup>-4</sup>	9.54 x 10 <sup>-5</sup>
250	9.76 x 10 <sup>-4</sup>	3.82 x 10 <sup>-4</sup>	1.14 x 10 <sup>-4</sup>

**Table 6.1—Diffusion coefficients of MSA at different concentrations.**



**Fig. 6.1—Diffusion coefficient of 5 wt% MSA as a function of inverse of temperature.**

## CHAPTER VII

### APPLICATION AND CONCLUSIONS

Acidizing a damaged formation using HCl is an efficient and cost effective method but at high temperature conditions, it is also associated with various drawbacks such as rapid rock dissolution, high corrosion rate, sludge formation tendency with asphaltene molecules, etc. Different organic acid solutions like formic, acetic and citric acid are used as an alternative to HCl for higher temperature acidizing jobs. These acid solutions have shown good field applications but they too have certain limitations which hinders its performance as stimulation fluid. Firstly, these acids are weakly dissociated and therefore have lower reactivity compared to HCl. Formic acid is among the strong organic acids and still its dissociation constant is just about 1.3%. Apart from this the reaction between formic acid and calcite generates calcium formate, which has very low solubility at higher concentrations. Furthermore, the use of formic acid also causes many environmental issues.

The focus of this study was to find the dissolution rate of MSA with calcite and to derive mass transport properties. MSA, being strong organic acid reacts with MSA dissolves calcite rock at the rate of  $10^{-6}$  cm<sup>2</sup>/s. The order of dissolution rate is synonymous with that of HCl. This information can be used by the engineers to design better well stimulation jobs. Also the at temperatures 73-250°F, the reaction of MSA with calcite was controlled by mass transfer up to 1,000 rpm at all concentrations of 5-20 wt%. The diffusivity of MSA was determined and reported at different temperatures (73-250°F) and

concentrations (5-20 wt%) of MSA. At 5 wt% MSA, the effect of diffusion on temperature followed the Arrhenius law and the activation energy and the pre-exponential constant for diffusion were found to be 30 KJ/mole K and 9.485 cm<sup>2</sup>/s, respectively.

## CHAPTER VIII

### FUTUREWORK

Since MSA is the new acid that is been tested for acidizing applications, there is numerous work that could be done to better understand the acid/reactions. Based on the findings presented in this work, further work could provide more comprehensive understanding of the reaction of MSA with calcite. The following are the research that could done

1. Dissolution rate studies with RDA should be conducted using Dolomite rock to study the dissolution rate profile of MSA with Dolomite.
2. Acid retardation capacity of MSA.
3. Acid sludge formation.
4. Solubility of calcium methanesulfonate under reservoir conditions.
5. Combination of MSA/HF for sandstone acidizing applications.

## REFERENCES

1. Alkattan, M., Oelkers E.H., Dandurand, J.L. et al. 1998. An Experimental Study of Calcite and Limestone Dissolution Rates as a Function of pH from – 1 to 3 and Temperature from 25 to 80 C. *Chemical Geology* **151** (1): 199-214. [http://dx.doi.org/10.1016/S0009-2541\(98\)00080-1](http://dx.doi.org/10.1016/S0009-2541(98)00080-1).
2. Baker, Simon C, Don P Kelly, J Colin Murrell. 1991. Microbial degradation of methanesulphonic acid: a missing link in the biogeochemical sulphur cycle (in.
3. Barmatov, Evgeny, Jill Geddes, Trevor Hughes et al. 2012. Research On Corrosion Inhibitors For Acid Stimulation. Proc.
4. Barton, P. and Vatanatham, T. 1976. Kinetics of limestone neutralization of acid waters. *Environmental Science & Technology* **10** (3): 262-266. <http://dx.doi.org/10.1021/es60114a010>.
5. Chang, F.F., Nasr-El-Din, H.A., Lindvig, T. et al. 2008. Matrix Acidizing of Carbonate Reservoirs Using Organic Acids and Mixture of HCl and Organic Acids. Presented at the SPE Annual Technical Conference and Exhibition, Denver, Colorado, USA, 21-24 September. SPE-116601-MS. <http://dx.doi.org/10.2118/116601-MS>.
6. Finšgar, F and Milošev, I. 2010. Corrosion behaviour of stainless steels in aqueous solutions of methanesulfonic acid. *Corrosion Science* **52** (7): 2430-2438. <http://dx.doi.org/10.1016/j.corsci.2010.04.001>
7. Finšgar, Matjaž, Ingrid Milošev. 2010. Corrosion behaviour of stainless steels in aqueous solutions of methanesulfonic acid (in *Corrosion Science* **52** (7): 2430-2438.
8. Fogler, H Scott, Kasper Lund, CC McCune. 1975. Acidization III—the kinetics of the dissolution of sodium and potassium feldspar in HF/HCl acid mixtures (in *Chemical Engineering Science* **30** (11): 1325-1332.

9. Fogler, H. S., K. Lund, C. C. McCune. 1976. Predicting the Flow and Reaction of HCl/HF Acid Mixtures in Porous Sandstone Cores (in.
10. Fredd, C.N. and Fogler, H.S. 1998c. The Kinetics of Calcite Dissolution in Acetic Acid Solutions. *Chemical Engineering Science* 53 (22): 3863-3874. [http://dx.doi.org/10.1016/S0009-2509\(98\)00192-4](http://dx.doi.org/10.1016/S0009-2509(98)00192-4).
11. Fuller, M.J. 2010. Method for Treating a Subterranean Formation, US Patent No. 20140076544 A1.
12. Gernon, M. 1999. Environmental benefits of methanesulfonic acid. Comparative properties and advantages. *Green Chemistry* 1 (3): 127-140. <http://dx.doi.org/10.1039/A900157C>.
13. Guin, James Aston, RS Schechter, IH Silberberg. 1971. Chemically induced changes in porous media (in *Industrial & Engineering Chemistry Fundamentals* 10 (1): 50-54.
14. Guthrie, J. P. 1978. Hydrolysis of esters of oxy acids: pKa values for strong acids; Brønsted relationship for attack of water at methyl; free energies of hydrolysis of esters of oxy acids; and a linear relationship between free energy of hydrolysis and pKa holding over a range of 20 pK units. *Canadian Journal of Chemistry* 56 (17): 2342-2354. <http://dx.doi.org/10.1139/v78-385>.
15. Heidenfelder, T., Guzmann, M., Witteler, H. et al. 2009. Methods of Increasing Permeability in Carbonatic Rock Formations with Alkanesulfonic Acids, US 7,638,469 B2, Dec. 29, 2009. United States: BASF SE.
16. Hoefner, ML, H Scott Fogler. 1988. Pore evolution and channel formation during flow and reaction in porous media (in *AIChE Journal* 34 (1): 45-54.
17. Levich, V.G. 1962. *Physicochemical Hydrodynamics*, Englewood Cliffs, New Jersey, Prentice-Hall.

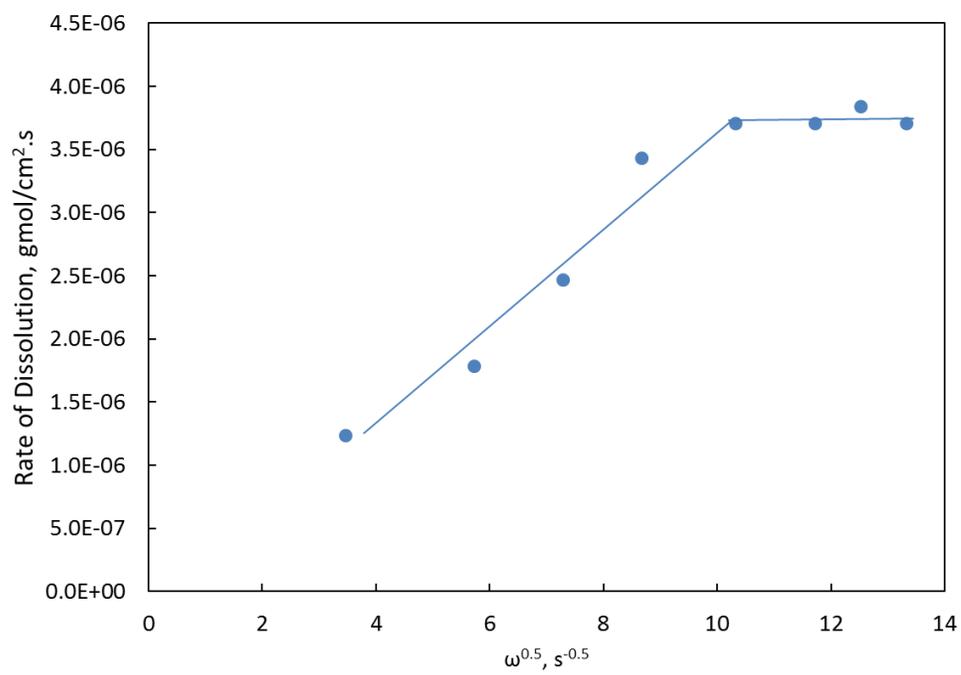
18. Lund, K., Fogler, H.S., McCune, C.C. et al. 1974. Acidization—II. The Dissolution of Calcite in Hydrochloric Acid. *Chemical Engineering Science* **30** (8): 825–835. [http://dx.doi.org/10.1016/0009-2509\(75\)80047-9](http://dx.doi.org/10.1016/0009-2509(75)80047-9).
19. Lund, Kasper, H Scott Fogler. 1976. Acidization--V: The prediction of the movement of acid and permeability fronts in sandstone (in.
20. Lund, Kasper, H Scott Fogler, CC McCune. 1973. Acidization—I. The dissolution of dolomite in hydrochloric acid (in *Chemical Engineering Science* **28** (3): 691-IN1.
21. Lund, Kasper, H Scott Fogler, CC McCune et al. 1975. Acidization—II. The dissolution of calcite in hydrochloric acid (in *Chemical Engineering Science* **30** (8): 825-835.
22. Newman, J. 1966. Schmidt Number Correction for the Rotating disk. *J. of Physical Chemistry* **70** (4): 1327-1328. <http://dx.doi.org/10.1021/j100876a509>.
23. Nierode, D. E., B. B. Williams. 1971. Characteristics of Acid Reaction in Limestone Formations (in.
24. Ortega, A., Nasr-El-Din, H.A., and Rimassa, S. 2014. Acidizing High Temperature Carbonate Reservoirs Using Methanesulfonic Acid : A Coreflood Study. Presented at the AADE Symposium on Fluids Technical Conference and Exhibition, Houston, Texas, 15-16 April. AADE-14-FTCE-3.
25. Plummer, L., Wigley, T., Parkhurst, D. 1978. The Kinetics of Calcite Dissolution in CO<sub>2</sub>-Water Systems at 5 Degrees to 60 Degrees C and 0.0 to 1.0 atm CO<sub>2</sub>. *American Journal of Science* **278**(2): 179-216. <http://dx.doi.org/10.2475/ajs.278.2.179>.
26. Rajeev, P, AO Surendranathan, Ch SN Murthy. 2012. Corrosion mitigation of the oil well steels using organic inhibitors—a review (in *J Mater Environ Sci* **3** (5): 856-869.

27. Williams, Bert B. 1979. *Acidizing fundamentals*, New York : Henry L. Doherty Memorial Fund of AIME, Society of Petroleum Engineers of AIME, 1979. (Reprint). <https://search.library.wisc.edu/catalog/999507027102121>.

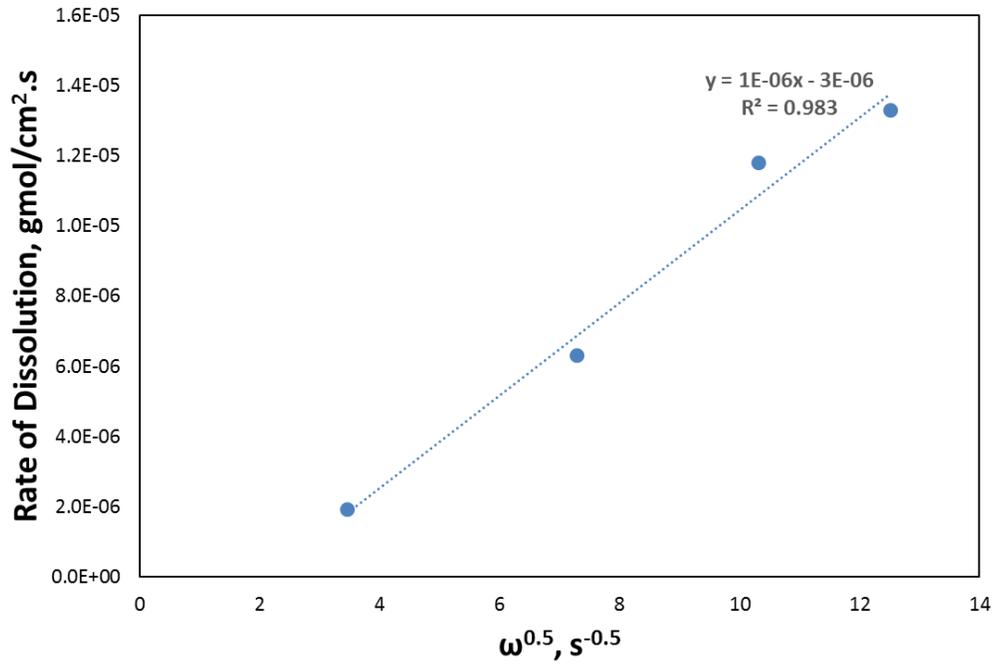
## APPENDIX

### Rotating Disk Experiments

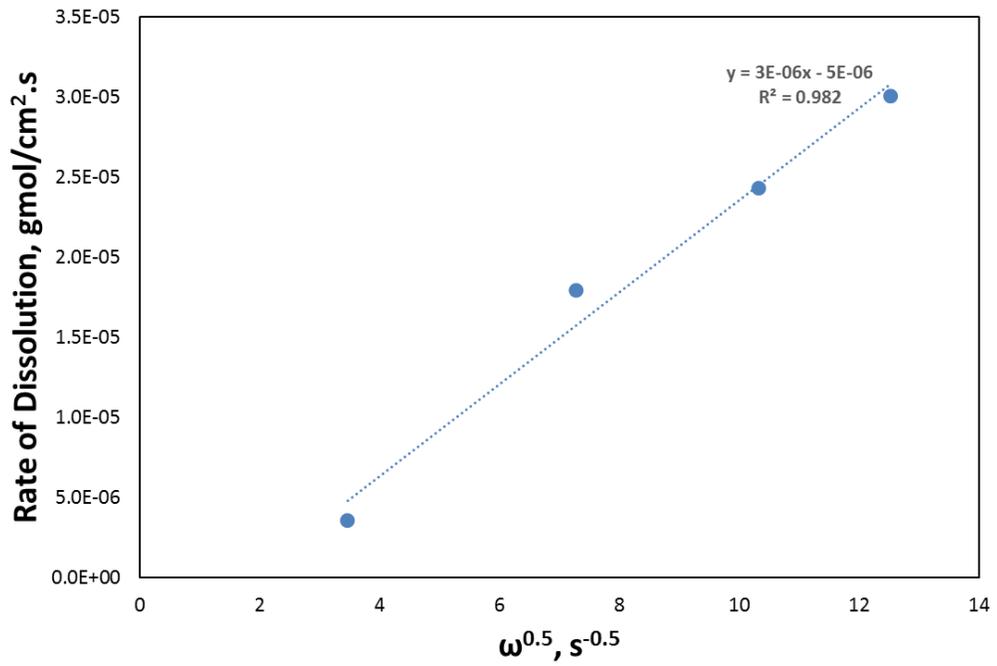
#### 5 wt% MSA at 73°F



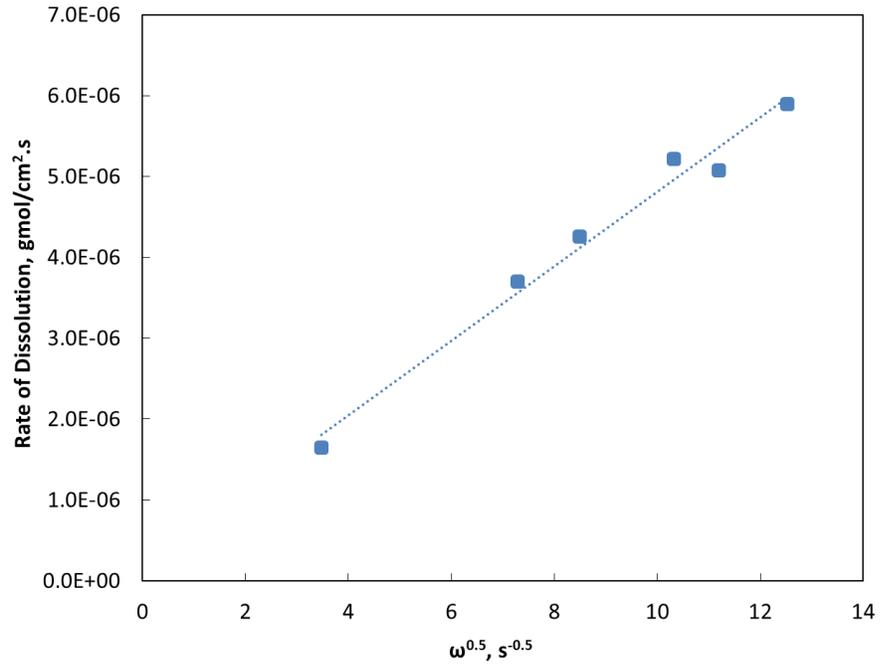
### 5 wt% MSA at 150°F



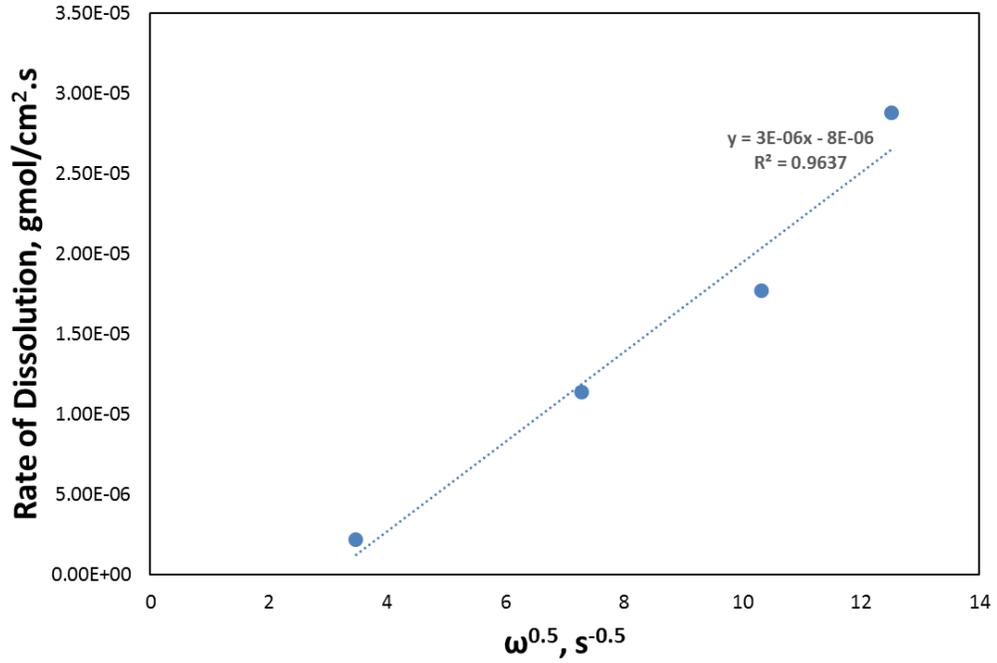
### 5 wt% MSA at 250°F



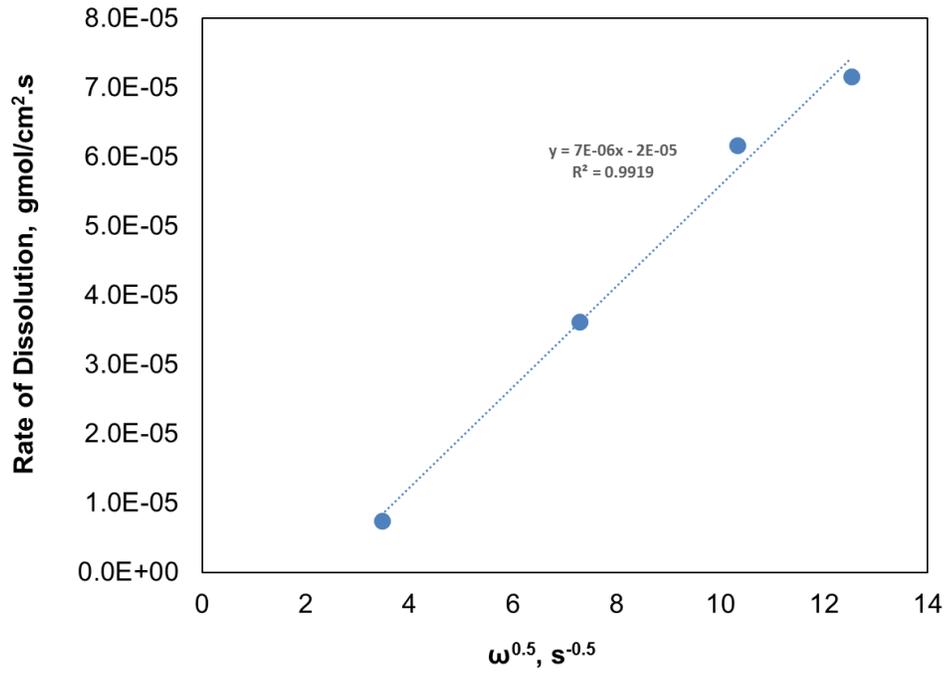
**10 wt% MSA at 73°F**



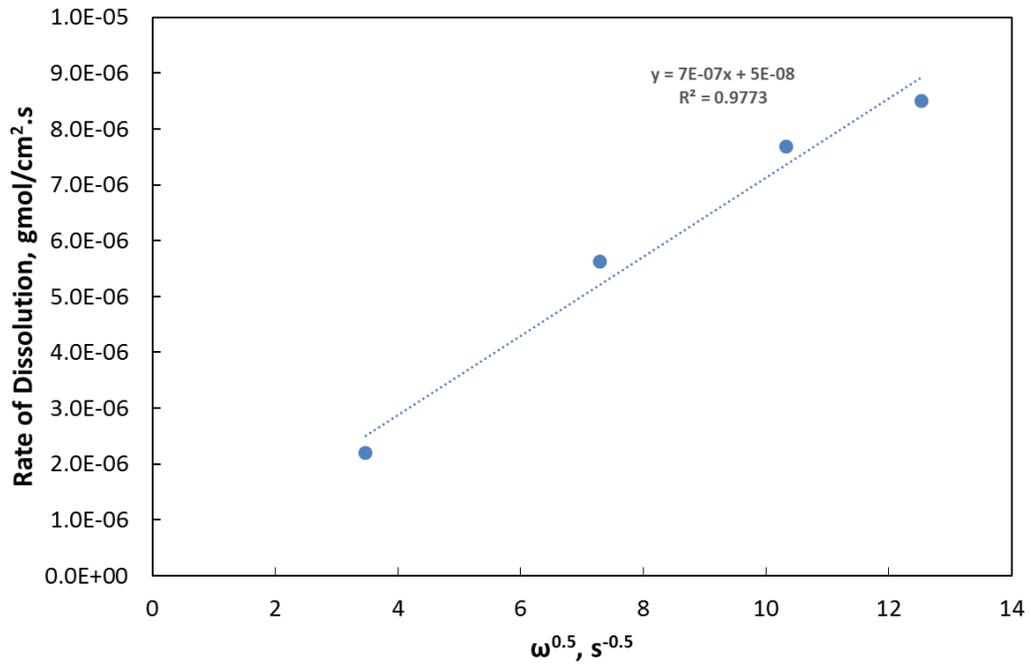
**10 wt% MSA at 150°F**



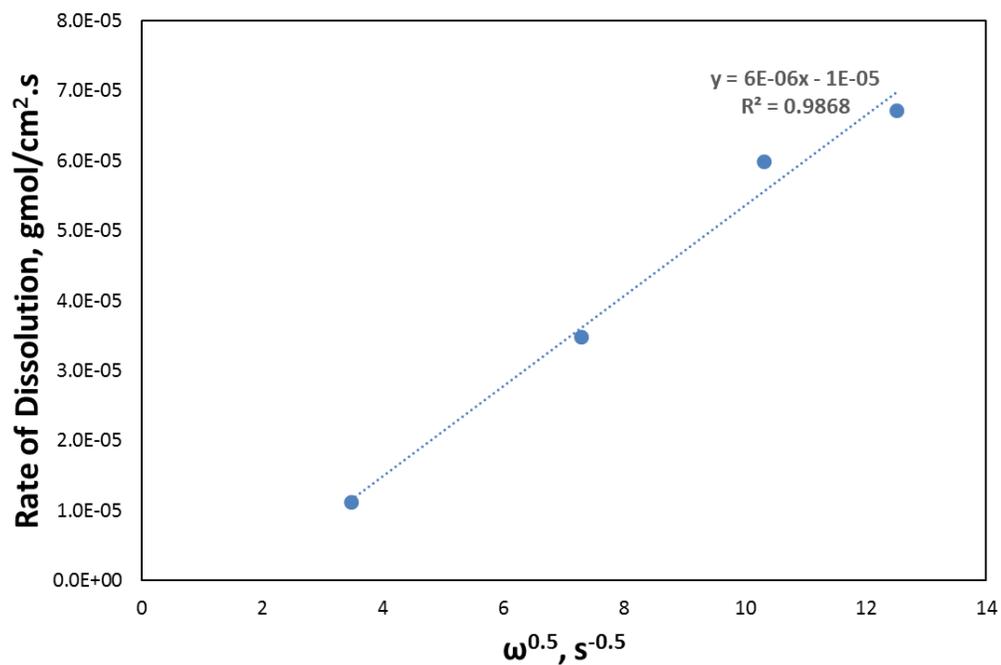
**10 wt% MSA at 250°F**



**20 wt% MSA at 73°F**



**20 wt% MSA at 150°F**



**20 wt% MSA at 250°F**

