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Abstract. The most common well intervention work to solve solid scale problem in oil production is a treatment to remove or inhibit the solid scale. Calcite ($CaCO_3$) and barite ($BaSO_4$) are two of the most common solid scale found in the oil well tubular and piping. Often, acid treatment such as hydrochloric acid is used to dissolve the solid scale. However, acid is highly corrosive and harmful to handle in the challenging environment of oilfield operation. A new generation of less corrosive solid scale dissolver includes functional group such as a carboxylic group due to its ability to chelate metals ions. This study utilised economical and non-toxic materials, monosodium glutamate (MSG), as the starting materials to synthesis solid scale dissolver with the carboxylic group as the main functional group presence. The double step acidification of MSG produces glutamic acid hydrochloride (GluCl). It is solid at room temperature and soluble in water makes it safer to transport and handle in the challenging environment of oilfield operation. Dissolution test shows that GluCl can dissolve more than 3000 ppm of calcium at a concentration of just 20g/L.

1. Introduction

Well completion involved pumping of high-pressure drilling fluid into the wellbore that can damage the surrounding formation in the reservoir. This damage will introduce solid particles such as sand and clay into the reservoir pores and reduce the oil flow towards the drainage area and block the drainage area [1]. The solid scale also might come from the precipitation of solids from produced water inside the well containing dissolved solids such as calcium, barium and iron [2-5]. One of the most common scale in an oil well is calcium carbonate [3, 6-8]. It was formed through the loss of CO_2 in the formation of water due to the drop of pressure lead to loss of carbonate acid that keeps the calcite dissolved [9, 10]. Barium sulphate is the most insoluble scale that can be precipitated from oilfield waters. It forms a hard scale which is extremely difficult to remove [11, 12]. The solubility of barium sulphate goes up with increasing temperature, pressure and salt content of the brine [11, 13, 14].

Acid such as hydrochloric acid (HCl) is commonly used to dissolve calcium carbonate scale or to improve the permeability of the well. However, acid treatment is known to cause significant damage to the well tubular and other equipment due to their corrosivity property [10, 15, 16]. Due to its corrosivity, acid is harmful to handle at a challenging environment in oil field operation. In solid scale

dissolution, a new generation of less corrosive dissolver utilized functional groups such as carboxylic acid and amine in the solid scale dissolution [17, 18]. Dissolver containing carboxylic and amine can reduce the reprecipitation of solid scale [19]. This study aims to investigate the potential of amino acid hydrochloride to be used as solid scale dissolver. An amino acid contains a carboxylic group and amine that can act as a ligand to bind with the metal ion of the solid scale [20-22]. Developing solid scale dissolver based on amino acid can be made less harmful to handle. The amino acid is an organic compound determined by the presence of carboxylic (-COOH) and amine (-NH$_2$) as its primary functional group with other functional group attached to its side chain [23, 24].

In this study, amino acid hydrochloride was synthesized from monosodium glutamate (MSG) as the main reactant for the synthesis of amino acid-based solid scale dissolver. MSG is the sodium salt of L-glutamic acid, abundant and naturally occurs amino [25, 26]. MSG produces mainly through the fermentation process of plant sources carbohydrates such as sugar cane and tapioca. MSG is relatively cheap to be used as a raw material due to its vast application in food production and domestic use as well as non-toxic to the environment. Figure 1 shows the molecular structure of MSG.

Figure 1. Molecular structure of monosodium glutamate (MSG). MSG contains one carboxylic group, one carboxylate ions and amine connected to the carbon chain.

2. Methodology

2.1 Acidification of Monosodium Glutamate

In the acidification of MSG, 33.822 g of MSG (0.2 mol) was dissolved in 150 ml of deionised water. The solution was continuously stirred using magnetic stirrer. About 16.56 ml of 37% HCl was added drop by drop into the solution and the white precipitate (glutamic acid) will start to form. An excess of 2 ml of HCl was then added. The mixture was continuously stirred 10 minutes. The stirring was stopped, and the glutamic acid allowed to precipitate for 12 hours. Once a supernatant can be observed, the water was separated by carefully pouring about 2/3 water from the supernatant and retaining the solid inside the beaker. Then, 100 ml of deionised water was added to wash the glutamic acid and allowed to precipitate again for another 30 minutes. Once a supernatant can be observed, the water was separated again by carefully pouring out the liquid. This process was repeated for three times. The remaining liquid after the third washing was separated using filter paper. The glutamic acid collected was dried in an oven at 60 °C until a constant weight was obtained (24-48 hours). The dried glutamic acid was weight to determines it's yield before analysed using Fourier transform infrared (FTIR) and compare with standard glutamic acid purchased from Sigma Aldrich. The mechanism of the reaction is shown in figure 2.
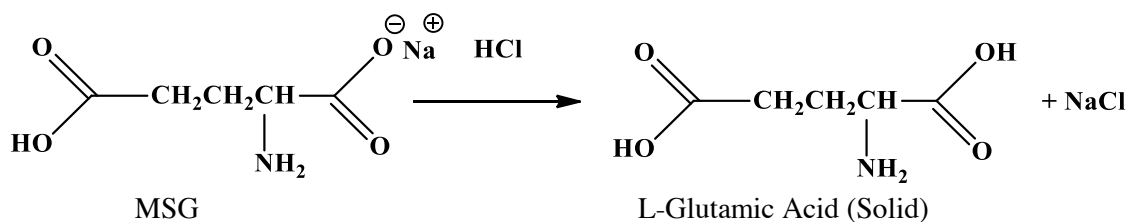
Figure 2 Reaction mechanism of acidification of monosodium glutamate to produce L-Glutamic acid.

2.2. Synthesis of glutamic acid hydrochloride

About 29.426g of glutamic acid (powdered) was mix with 100 ml of deionised water and continuously stirred for 10 minutes. Once a homogeneous mixture was obtained (white milky colour) about 16.56 ml of hydrochloric acid was added drop by drop to the mixture. The mixture will turn into a colourless solution. The solution was then continuously stirred for another 1 hour. If any undissolved solid was observed, the solution will be filtered with filter paper. The solution was evaporated under vacuum using rotary evaporator at 60 °C until all the liquid has evaporated. The solid product was collected and transferred into a beaker and then dried in a vacuum oven at 60 °C until the mass of the product remains constant (24-48 hours). The mechanism of the reaction was shown in figure 3. The final product was analysed using FTIR. Pycnometer was used to determines its density and the melting point was analysed using Buchi Melting Point M-565 (Switzerland) with temperature range was set from 60 °C to 250 °C at a heating rate of 10 °C/min.
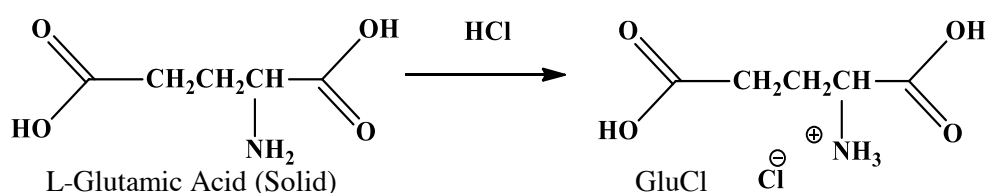

Figure 3 Synthesis mechanism for the production of glutamic acid hydrochloride form acidification of L-glutamic acid with hydrochloric acid.

2.3. Dissolution Test

Two different solutions of 20g/L of GluCl solution was first prepared. The first solution was prepared using only deionised water mixed with GluCl. The second solution was prepared by adding 0.25 M of potassium hydroxide (KOH) solution to adjust the pH to more than 11. The temperature changed on the solution during the preparation was measured. The pH of the solution was measured using Mettler Toledo pH meter. 2 g of calcite and barite was measured each and put in separate centrifuge tubes. 40 ml of the first batch of GluCl solution as poured into each of the centrifuge tubes. The tubes were slightly shaken to mix the contents inside. The tubes were then put into an oven at 60 °C for 24 hours. After 24 hours, the liquid from the tube was collected and filtered using syringe filter (0.4 μ) before being analysed using inductive coupled plasma-optical emission spectroscopy (ICP-OES). The steps were repeated by using the second solution of GluCl solution.

3. Result and Discussion

L-glutamic acid produce from acidification of MSG was analysed using FTIR to compare with standard glutamic L-Glutamic acid purchased from Sigma Aldrich. Figure 2 shows the infra-red spectroscopy of L-glutamic acid produces from the acidification of MSG compared with standard L-glutamic acid. The stretch of carboxylic acid in L-Glutamic acid occurs wavelength 3300 to 2500 cm^{-1} and amine at 1650-1580 cm^{-1}. Product of precipitation of L-glutamic acid from MSG is comparable with standard L-glutamic acid in which both products show the main peak for carboxylic and amine.
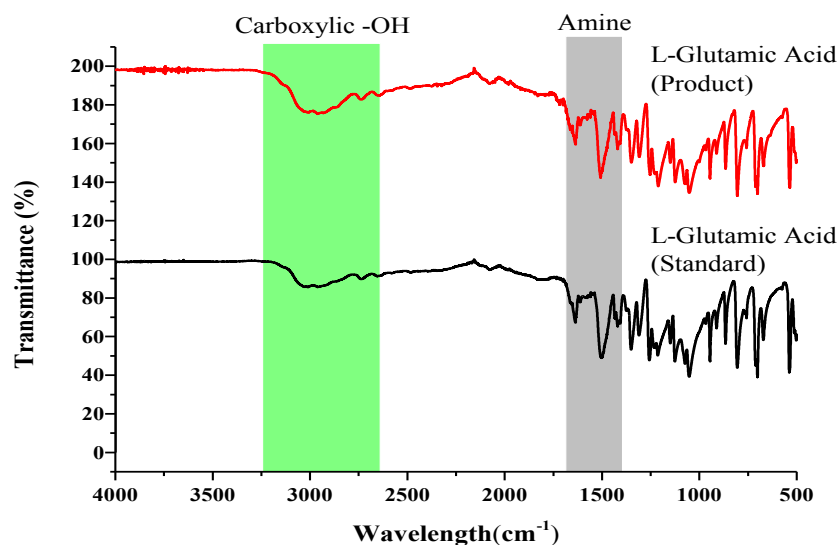
Figure 4 FTIR spectroscopy of L-Glutamic acid product from acidification of MSG compared with standard L-Glutamic acid purchased from the Sigma-Aldrich.

CHNS analysis was conducted on the product to determine the percentage of the element present in the product. Theoretically, L-glutamic acid should contain 40.82 % of carbon 43.57 % of oxygen, 9.52 % of nitrogen and 6.12 % hydrogen. CHNS analysis (table 1) shows that L-glutamic acid produce from acidification the elemental percentage is close to theoretical value with 38.54 % carbon, 9.01 % nitrogen, and 6.16 % hydrogen. This result is close to the theoretical percentage of an element in L-glutamic acid.

Table 1 CHNS analysis of L-glutamic acid produce from acidification of monosodium glutamate.

Element	Theoretical %	CHNS %
Carbon	40.82	38.54
Nitrogen	9.52	9.01
Hydrogen	6.12	6.16
Sulphur	-	0.19

L-glutamic acid produce form acidification of monosodium glutamate was acidified to produce glutamic acid hydrochloride (GluCl). In this reaction, hydrochloric acid protonates amine group of L-glutamic acid resulting in amino acid with amine salt. This reaction yields $70.08 \pm 1.621\%$ of the product. Glutamic acid hydrochloride (GluCl) is solid at room temperature with melting point 219.68 ± 0.97 °C and completely miscible in water. The density of GluCl is 0.5755 g/cm^3. The properties of glutamic acid hydrochloride were summarised in table 2. Figure 5 shows the infra-red spectrum of glutamic acid hydrochloride obtained from this study compares with L-glutamic acid. Both compounds show the peaks for carboxylic -OH bond and amine. However, glutamic hydrochloride has broad aliphatic primary amine at wavelength 3500 cm^{-1} that are not present in L-glutamic acid. In glutamic hydrochloride, amine act as cations consists of three hydrogens attached compare to two in L-glutamic acid. This probably increases the presence of -NH stretch in the infrared spectroscopy. In addition, the peak for amine salt can be observed at wavelength 1600 cm^{-1} in glutamic acid hydrochloride [27].

CHNS analysis of the compound in table 3 shows that it has 29.8% carbon, 9.01 % nitrogen and 6.16 % hydrogen. This value is close to the theoretical value calculated for GluCl with sulphur detected as impurities. EDX analysis results in table 4 show that the product contains 43.13 % carbon,

39.42 % oxygen, 9.76 % nitrogen and 17.27 % chlorine. This value is close to theoretical value except for carbon that has a higher percentage. The presence of chlorine close to theoretical percentage indicating successful reaction with a small amount of sodium detected as impurities.

Table 2 Properties of glutamic acid hydrochloride synthesised form acidification of L-Glutamic acid.

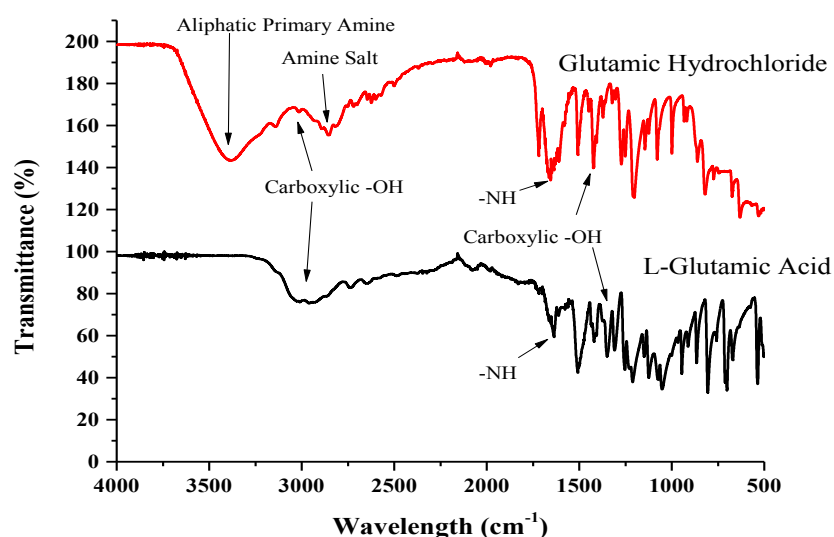| Glutamic Hydrochloride	
Yield	$70.08 \pm 1.621\%$
Appearance	White Crystalline Powder
Melting point	219.68 ± 0.97 °C
Solubility	Soluble in water
Density	0.5755 ± 0.0087 g/cm3

Figure 5 FTIR spectroscopy of glutamic hydrochloride compare with L-glutamic acid

Table 3 CHNS analysis of glutamic acid hydrochloride

Elements	Theoretical %	CHNS %
Carbon	32.71	29.8
Nitrogen	7.63	9.01
Hydrogen	5.45	6.16
Sulphur	-	0.31

Table 4 EDX analysis of glutamic acid hydrochloride

Element	Theoretical %	EDX %
Carbon	32.71	43.13 ± 0.804
Oxygen	34.89	39.42 ± 0.649
Nitrogen	7.63	9.76 ± 5.570
Chlorine	19.32	17.27 ± 0.286
Sodium		0.18 ± 0.056

The salt produced was evaluated for dissolution capability for two types of solid scale; calcium carbonate ($CaCO_3$) and barite ($BaSO_4$). To control the pH, potassium hydroxide (KOH) was used to control the pH of the solution. The amount of KOH used to control the pH for 500 ml of solution is between 5-7 g. Therefore, the solubility of both scale in 0.25M of KOH solution was first determined. Albeit KOH is used as one of the synergist in barite dissolution [12], the result shows that at a concentration of 0.25M, KOH does not dissolve calcite and barite. Thus, the used of KOH for pH control will not significantly affect the dissolution result. As shown in table 5, GluCl 20g/L solution used in the dissolution have pH value at 1.69. During the preparation of the solution, no increase in temperature was recorded. At pH 1.69. The GluCl solution can dissolve up to 3865 ppm of calcium in 24 hours at 60 °C and less than 5ppm of barium. Increasing the pH of the solution to 11.69 reduce the dissolution of calcite to just 14.62 ppm and barite to 3.67 ppm.

Table 5 ICP-OES result for the concentration of calcium and barium ion in the solution of GluCl after dissolution for 24 hours at 60 °C

pH	Solid Scale	Metal Ion Tested	Metals ions Detected (ppm)
1.69	CaCO3	Ca^{+2}	3865 ± 21.213
	BaSO4	Ba^{+2}	4.794 ± 0.147
11.69	CaCO3	Ca^{+2}	14.62 ± 0.007
	BaSO4	Ba^{+2}	3.672 ± 0.464

4. Conclusion

This study has synthesis ionic salt solid scale dissolver; glutamic acid hydrochloride (GluCl). GluCl ionic salt produced is soluble in water. Based on the dissolution result, GluCl is a good dissolver for calcite as it can dissolve more than 3000 ppm of calcite at low concentration. Barite is known as the most difficult solid scale to dissolve. In this study, GluCl could not dissolve barite. GluCl produced is in the solid form which is easier to transport and handle in the challenging environment of an oil filed operation in comparison to liquid acid.

Acknowledgements

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