Inhibition of Naphthenates Emulsion Soaps Chemical EOR using Synthesis Compound Derived from Fatty Hydrazide.

N. Borhan¹,², A. Ramli²
¹Petronas Research Sdn Bhd, Lot 3288 & 3289, Off Jalan Ayer Itam, Kawasan Institusi Bangi, 43000, Kajang, Selangor
²Fundamental and Applied Sciences Department, Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Perak, Malaysia.

noorazlenawati_borhan@petronas.com

Abstract. Naphthenates soaps emulsion generated from alkaline (A), surfactant (S) and polymer (P) flooding were studied with crude oil contained amphiphilic carboxylic acids, RCOOH from Malaysian oilfield. These naphthenic acids were characterised using high-resolution fourier transform ion-cyclotron resonance mass spectroscopy (FTCIR-MS). Alkaline Na₂CO₃ resulted in increase in pH of produced water to between pH 9 to 11 and generates in-situ oil-rich colloidal dispersion ultralow interfacial tension (IFT) character of sodium carboxylate soaps emulsion. Predictive measurement and inhibition were evaluated using new naphthenate inhibitor (NI)-demulsifier synthesized from fatty hydrazide. The structures of the synthesized compounds have been established by FTIR, ¹H NMR, ¹³C NMR, and mass spectrometry (LCMS/MS). Inhibition and demulsification properties have been evaluated at operating parameters such as produce water cut level, ASP concentration and temperatures under dynamic testing condition using Multifunctional Mini Flow Loop (MMFL)³⁴.

1. Introduction
During fluid flow from reservoir to surface of chemical enhance the oil recovery (CEOR), the produced water contains some of the alkaline (A), surfactant (S) and polymer (P) carry over in the form of oil in water (O/W) and water in oil (W/O) microemulsion. This microemulsion contains of sodium carboxylate soaps or known as naphthenates soaps. Naphthenic acids (NAs) is a generic name used for all organic acids present with homologous by a general formula CₙH₂₃₂₄O₃ where n represents the carbon number and Z is an even, negative integer corresponding to hydrogen deficiency mainly due to ring formation in the structure [1]. Double bond equivalences (DBE) is a value equivalent to the number of double bond in the molecular structure which is similar to the Z number series. NAs varies in molecular weight (Mw) with low Mw of m/z ~200 to 700; Z = -2, -4, -6 group representing alkenic acids of DBE of 1 and high Mw m/z of 1220 to 1310 representing DBE of 4 and 6 saturated rings which are also referred as “ARN”, 4-proton acid [2]. High pH system of sodium carbonate (Na₂CO₃) component will dissociate the heavier NAs and long-chain carboxylic acids. The NAs, RCOO⁻ moieties become reactive towards metal cations in the water phase and formed complex with calcium (Ca²⁺) and sodium ions (Na⁺) forming (RCOO)₂Ca and RCOONa at oil-water interface through the formation of layered lamellar liquid crystalline films [4]. Bicarbonate ions (HCO₃⁻) tend to stabilise the oil-water interface as the species [Na(HCO₃)]⁻ whereby enhanced of concentration of HCO₃⁻ ions around the oil-water interface will promote the combination of Na⁺ and HCO₃⁻ ions together...
[5]. Increase in the total concentration of ionized NAs, RCOO⁻ at the interface would decrease in interfacial tension (IFTs) due to electrical double layer effect and increase in dilatational elasticities [6]. Micelles formed in the water phase (i.e. O/W emulsion) and reverse micelles in the oil phase (i.e. W/O emulsion). W/O emulsions prevents droplet coalescence and adversely impact the crude oil dehydration and saleability parameter of basic sediment and water (BSW).

Chemical methods by blending of naphthenate inhibitors (NIs) and demulsifiers is common mitigation approach for emulsion resolution as well as to accelerate the crude oil dehydration process. NIs inhibits the surface active properties which congregate at oil-water interface and form a layer that prevents the interactions between protonated NAs and cations (i.e. Na⁺ and Ca²⁺) in the water phase. Demulsification is an emulsion reversal process by destructing and reducing the thickness of oil-water interfacial film, allowing the W/O droplets to coalesce. In the structures of many demulsifiers, the hydrophilic parts are composed of oxyethylene, hydroxyl, carboxyl, or amine groups, while the hydrophobic parts contain alkyl, alkyphenol, or oxypropylene groups. The hydrophobic and hydrophilic characters of a demulsifiers determine its effectiveness in W/O emulsion destabilisation, as well as O/W minimization [7-9]. In this paper, we report the synthesis of polymeric fatty acid ester amide compound as NI-demulsifier.

2. Experimental
2.1. Extraction of naphthenic acids from crude oil and mass spectrometry
Naphthenic acid (NAs) were extracted using Ion Exchange Resin (Acid-IER) methods. The mechanism reaction of extraction used QAE Sephadex A-25 which is a sugar base resin (poly-1,6-glucose) with the diethyl-(-2-hydroxypropyl) aminoethyl ion exchange group. The extracted NAs samples were analyse using FTICR-MS from Thermo Fisher Scientific, 2D Linear Quadrupole Ion Trap Fourier Transform (LTQ-FT) mass spectrometry (positive ionization mode ESI-MS) Ultra 7 Tesla system.

2.2. Synthesis of polymeric fatty ester amide compound

0.02 mole of maleic acid anhydride was reacted with 1.175 mole of methanol under esterification proses at 80 to 90°C. The produced intermediate compound of monomethyl ester, 2-Butenedionic acid (2Z)- was then reacted with 0.005 mole of palm fatty hydrazide to produce final compound in a 250mL 3-neck flask fitted with den stark apparatus. 100 mL mixture of methyl isobutyl ketone (MIBK) and N,N-dimethylformamide (DMF) at 1:1 ratio was used as catalyst.

2.3. Characterization of the synthesized polymeric fatty ester amide compound

The structure of the synthesized compound was recorded using H NMR and ¹³C NMR on a Bruker 400 MHz SB Ultra Shield™. The NMR spectra were recorded in CDCl₃ and chemical shifts recorded were internally referenced to TMS (0 ppm). Fourier transform infrared (FT-IR) spectra was obtained using a Perkin Elmer Spectrum® 400 FT-IR spectrophotometer. Mass spectra were obtained on LCMS/MS-AbSciex Qtrap 3200 with scan range mass 50 to 500, turbo spray with positive electron spray ionisation (ESI) and detector voltage of 2700 V.

2.4. Dynamic condition testing by MMFL™

The dynamic flow loop test is shown in Figure 1. Tests were carried out at 60 °C and 4.5 bar with a 40% water cut off match field separator conditions. Crude oil and brine were injected into a mixing cell equipped with a sealed homogeniser operating at 13,500 rpm. The combined fluids then flowed from the mixing cell through the two in-line filters. The first was a coarse filter/baffle and the second was a 7 µm sintered metal filter. The differential pressure (dP) across the fine filter was measured and plotted, allowing assessment of the viscosity of the fluids and any blockages arising from solids formation. The fluids then entered a glass separator where the oil/brine interface and any emulsion formed were observed and photographed. The entire apparatus is housed inside an oven and pressurised to replicate the conditions in a low-pressure separator in the field.
Figure 1: Schematic of the MMFL™

Table 1 shows the properties of the crude oils NAs while Table 2 shows the brine compositions used in this work. Table 3 shows the composition of the ASP injection water used.

Table 1: Details of crude oils

| Field | TAN (mg KOH/g) | Monoprotic acids                        |
|-------|----------------|----------------------------------------|
| A     | 0.50           | Saturated acyclic (DBE=1) and higher DBE (4-6) species |

Table 2: Details of brine compositions

| Ion (mg/L) | Na  | Ca  | Mg  | K  | Ba | Sr  | Fe  | SO₄  | HCO₃  | Cl  |
|------------|-----|-----|-----|----|----|-----|-----|------|-------|-----|
| Field A (PW) | 3,429 | 10  | 26  | 38 | 0  | 1.4 | 2.4 | 36   | 4,339 | 3,053 |

a Ba, Fe and SO₄ were omitted

Table 3: Details of ASP injection water

| Component                  | Concentration  |
|----------------------------|----------------|
| Sodium carbonate (alkali)  | 1 wt%          |
| Surfactant B                | 0.5 wt%        |
| Polymer A                   | 2,000 ppm      |
| Diluent                     | 16,000 ppm NaCl brine |

3. Result and Discussion

3.1 Naphthenic acids mass spectrometry

The crude oil contains a broad range of lower Mw acids, with a small fraction of moderate molecular weight (650 – 900 Da) acids present (Figure 2a). DBE analysis of monocarboxylic acids reveals a mixture of saturated, acyclic (DBE = 1, Cᵡ₋ₓ) and higher DBE (2-3 at Cₓ₋ₓ and 4-6 around Cₓ) acids (Figure 2b).
Figure 2: Mass spectroscopy chromatogram (a) and DBE of O2 acids, RCO₂H class (b)

Table 4: NAs distribution from crude oil A

| No of ring | Z  | % Rel Ab. O2 Class |
|------------|----|-------------------|
| 0          | 0  | Saturates         | 9.9 |
| 1          | 2  | Monocyclic        | 19.5|
| 2          | 4  | Dicyclic          | 15.1|
| 3          | 6  | Tricyclic         | 7.5 |
| 4          | 8  | Tetracyclic       | 14.4|
| 5          | 10 | 5 DBE             | 11.8|
| 6          | 12 | 6 DBE             | 6.0 |
| 7          | 14 | 7 DBE             | 6.3 |
| 8          | 16 | 8 DBE             | 3.9 |
| 9          | 18 | 9 DBE             | 2.6 |
| 10         | 20 | 10 DBE            | 2.1 |
| 11         | 22 | 11 DBE            | 1.1 |

3.2 Characterization of the polymeric fatty acid ester amide compound

The FTIR spectra (Figure 3) of fatty acid ester amide in the waxy solid state shows absorption bands at 2850 and 2917 cm⁻¹ corresponding to stretching of long alkyl chain of asymmetric and symmetric stretch vibration of CH₃, CH₂ and CH. The asymmetric vibrations νas(N-H) group stretching bands for secondary amide appears at 3475 cm⁻¹ and symmetric vibrations νs(N-H) at 3233 cm⁻¹. A broad intense band of symmetric stretching vibrations of C=O amide II resonated at 1598 cm⁻¹ and a weak vibration of C=O ester at 1703 cm⁻¹. Absorption band of C-N stretching is observed between 1024-1059 cm⁻¹. The -CH₃ absorption band is observed at 1380 cm⁻¹. C=C absorption band is observed at 1467 cm⁻¹ and weak C-O band of ester is observed at 1171 cm⁻¹.
The proton and carbon chemical shift assignment (Figure 4a and 4b). $^1$H NMR (400 MHz, CHLOROFORM-d) δ ppm = 0.88 (#C19, 31, m, 6H), 1.20 (#C26, 27, m, 3H), 1.23 (#C18, 20, 21, 22, 23, 24, 25, 28, 29, 30, 27, s, 19H), 1.59 (#C17, m, 2H), 2.28 (#C16, m, 3H), 2.90 (#C13, m, 3H), 5.81 (#C8a,9a, br s,3H), 7.32 (#N3a, m, 1H), 7.99 (#N2, s(AA'BB'), 4H). $^{13}$C NMR (101 MHz, CHLOROFORM-d) δ ppm = 13.59 (#C31), 21.93(#C30), 24.11 (#C17), 28.83 (#C20), 28.88 (#C19), 28.99 (#C18), 29.13 (#C21), 29.17 (#C26), 29.81 (#C22,23,24,25), 30.89 (#C27), 31.40 (#C28), 35.16 (#C29), 35.98 (#C16), 52.24 (#C13), 131.18 (#C9), 134.36 (#C8), 164.56 (#C5), 165.16 (#C10),166.69 (#C1).
Figure 5: Pathway of the ESI mass fragmentation of synthesis compound

3.3 NI-Demulsifier performance by MMFL™

The differential pressure shows the influence of high viscosity emulsion fluids in the conditions of high pH between 9 to 9.5 (Figure 6a). As expected, higher Mw NAs with 3, 4 and 5 membered rings will be protonated and soluble towards water affinity to form micelles of W/O and O/W emulsions. Increasing the pH causes higher charges layers and more water soluble stoichiometry, whereas more branched and rigid acid structures cause steric hindrance, which may counteract in formation of metal naphthenates. The drop in differential pressure after injection of 10 ppm of NI-demulsifier for 2 hrs duration shows sustainability performance overtime where lesser injection rate would be implemented in demulsifier injection system at oilfield offshore surface facilities (Figure 6b).
Figure 6: Differential pressure of produced ASP ratio PW: ASPW (80:20), pressure = 4.5bar, temperature = 60°C, water cut = 40% before treatment (a) and after treatment (b)

4. Conclusion

The NAs crude oil expected to produce sodium carboxylate-stabilised emulsions in the laboratory when mixed with its PW under current field conditions and with addition of ASP injection water exacerbated the emulsion formed. The polymeric fatty acid ester amide compound synthesized is able to dehydrate crude oil under the ASP tests. Lower concentrations of synthesized polymeric fatty acid ester amide compound show good performance as NI-demulsifier.
References

[1] Zhao, B., Currie, R., & Mian. H, 2012 Catalogue of Analytical Method for Naphthenic Acids Related to Oil Sands Operations

[2] M. M. Ahmed, and K. S. Sorbie, 2009 SPE 121633 Spectroscopic determination of naphthenic acid composition from various calcium naphthenate fields deposits SPE International Symposium on Oilfield Chemistry Woodlands, Texas, USA

[3] Grbović, Ljubica., Pavlović, Ksenija., Prekodravac, Bojana., Kevrešan., Milić, Jelena., Ćirin-Novta, Vera., Kuhajda, Ksenija., Popsavin, Mirjana., 2012 Fractionation of complex mixtures of naphthenic acids, their characterization and biological Journal of the Serbian Chemical Society vol. 77 (2) pp. 147-157

[4] Nordgård, E. L., Hanneseth, A.-M. D., & Sjöblom, J. 2010 Inhibition of Calcium Naphthenate. Experimental Methods to Study the Effect of Commercially Available Naphthenate Inhibitors. Journal of Dispersion Science and Technology 668-675

[5] Nichols, D.A, Rosário, F.F, Bezerra, M. C.M, Gorringe, S.E, Williams, H.L, & Graham, G.M., 2014 Calcium Naphthenates in Complex Production Systems-Evaluation and Chemical Inhibition Challenges SPE 169756 SPE International Oilfield Scale Conferences and Exhibition Aberdeen UK

[6] Kang, W. L.; Liu, Y.; Qi, B. Y.; Liao, G. Z.; Yang, Z. Y.; Hong, J. C. 2000 Interactions between alkali surfactant polymer and their effects on emulsion stability. Colloid. Surf. A 175, pp. 243–247.

[7] J. Wu, Y. Xu, T. Dabros, and H. Hamza, 2003 Effect of demulsifier properties on destabilization of water-in-oil emulsion Energy & Fuel 17, pp. 1554-1559, 2003

[8] Z. Zhang, G. Y. Xu, F. Wang, S. L. Dong, and Y. M. Li, 2004 Characterization and demulsification of poly (ethylene oxide)-block-poly (propylene oxide)-blockpoly(ethylene oxide) copolymers J. Colloid Interface Sci, 277 pp. 464-470

[9] A. A. Atta, H. I. Al-Shafy, and Z. M. Mohamed., 2011 Application of hydrophobically modified water-soluble polyacrylamide conjugated with poly(oxyethylene)-copoly (oxpropylene) surfactant as emulsifier,” Polym. Adv. Technol., 22 pp 1879-1887

Acknowledgments
Authors would like to thank PETRONAS Research Sdn Bhd personnel who directly or indirectly involved in this research. Technical guidance provided by Intan Khalida Salleh and EOR Value Assurer (VA) by Dr Jamal Mohamad M Ibrahim and lastly the authors also wish to thank PETRONAS Management for their permission to publish this paper.