Development of simmultaneous quantification of non-ionic surfactant in chemical flooding using mobile $^1$H NMR

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Abstract. The injection of surfactant is potential to be lost during the process due to the adsorption of surfactant into the core. It is therefore crucial to analyzed the concentration of surfactant before and after injection to the core. Many methods are developed for determining the content of surfactant using UV-Vis Spectrophotometer by utilizing the chromophore group of the chemical. In this study, quantification of nonionic surfactant that absent of chromophore group was performed using a combination of mobile Nuclear Magnetic Resonance (NMR) with Solid Phase Extraction (SPE). SPE was used to extract the samples that dissolved in water, whereas NMR was used to identify the levels of nonionic surfactants that dissolved in deuterized solvents. Internal standard chemical was added to the sample to verify the concentration of samples. As a stationary phase was SPE C-18 and eluent was methanol, ethyl acetate, and n-hexane. Furthermore, the SPE results were measured using mobile $^1$H NMR 43 MHz with selected solvents namely deuterated chloroform (CDCl$_3$) and internal standard Dimethyl Formamide (DMF). Optimization results for determination of surfactant concentration up to 0.5% w/w was using the C-18 stationary phase, mobile phase methanol, ethyl acetate, and n-hexane.

1. Introduction

Today, petroleum production has diminished due to reduced natural pressure from the reservoir. But the amount of oil produced from natural pressure is still low than the amount of oil that is available. Therefore, for optimal harvest subsurface reservoir due to reservoir conditions, specific methods can be considered. The injection process chemicals such as alkalis, polymer and surfactant are concerned that the displacement of the reservoir oil below the surface. In this method of alkali impressing adsorption, has an important role in improving the efficiency of the injection system. Also, in this method of polymer, the improvement of mobility, and Surfactants reduce the surface tension [1].

The increase in oil recovery from reservoir hydrocarbon production has challenges to the economic costs of exploration in oilfield development, it is very important to learn [2, 3]. One of the most effective methods to increase oil recovery, adding chemicals such as surfactants, alkaline and polymer reservoir hydrocarbon production, is in order EOR operations. This material may individually or together, are added to water flooding [4,5]. In chemical flooding, the use of alkalis, surfactants, and polymers is strongly influenced by several factors such as reservoir rock, formation fluid properties and temperature of the reservoir. This material can be injected separately or together. ASP method is a cost-effective method and conventional in this operation [6,7].
The presence of surfactants in the injection solution can reduce the oil saturation, reservoir remains, have the a favourable effect. Surfactants consist of three categories based on the charge on their polar groups: anionic, cationic and non-ionic. Anionic surfactants, of surfactant is effective in the injection material, a chemical flooding the system because this material has a relatively low absorption are the rock the formation [8]. Study of surfactant adsorption on reservoir rock is very important. This determines the concentration which causes a decrease in the performance of the surfactant in the reservoir. So far, the most applied surfactant and laboratory work is ionic surfactant. Detection of the results of the ionic surfactant adsorption test has been done with extraction techniques using organic reagents.

Using the results of the reaction in the form of a colored solution, the concentration of the sample can be tested using UV-Vis instruments. In contrast to nonionic surfactants which are difficult to react with certain reagents to produce a colored solution, so the concentration test cannot be carried out using a UV-Vis instrument. Therefore, the development of a test method for determining the concentration of nonionic surfactants was carried out. This method can be applied in determining the concentration of surfactant from core-flooding results for the study of kinetic adsorption from surfactants. Therefore, detector or instrument is needed that can detect compounds that do not have chromophore groups such as LSD or NMR instruments. NMR is a well-established quantitative tool in the fields of chemistry, biology, medicine and petroleum [9-11]. The electronic performances of NMR spectrometers are very stable. Spectra of a stable or standard sample stored in a sealed tube shows a reproducible integral area for a few years with a variation of less than 1.0%. During an NMR experiment, there is no chance of any contamination, dilution, or interaction with the detector, so the probe-head permits repetition of experiment on a sample after a long time with excellent reproducibility. For example, it is used in pharmaceuticals for purity analysis of drugs [12-13] and in food science for selective quantification of constituents [14-17].

In this study, we developed quantification of nonionic surfactant that absent of the chromophore group was performed using a combination of mobile NMR with Solid Phase Extraction (SPE). SPE was used to extract the samples that dissolved in water, where NMR was used to identify the levels of nonionic surfactants that dissolved in deuterated. Nonionic surfactant concentration test method using benchtop 1H Nuclear Magnetic Resonance (NMR) measurement in water solution at the ppm-level. We have established the feasibility of Benchtop 1H NMR in combination with solid-phase extraction (SPE) for crude oil in water analysis at the ppm level of detection [18]. The methodology uses a solvent system of 0.3% w/w DMF in Chloroform-D1 (CDCl₃) that provides an internal 1H NMR reference.

2. Materials and methods

2.1. Optimization of solid phase extraction (SPE) techniques for nonionic surfactants. The surfactant solution was made with a concentration of 0.1% w/w using injection water. Furthermore, the solution is passed in SPE tube (d = 0.72 cm) that has been filled in the stationary phase (C-18) that varied height (1 cm; 1.5 cm and 2 cm). Eluent used is Methanol (MeOH), Ethyl acetate (EtOAc), and n-Hexane (1 mL, 4 mL and 4 mL). The extraction results was evaporated to remove the solvent used. Further testing Chromatography Thin Layer (TLC) using the eluent Hexane and Ethyl Acetate (8: 2).

2.2. Surfactant measurement of extraction results with SPE technique

The extracted sample using the SPE technique was measured by Benchtop 1H NMR 43 MHz with chloroform (CHCl₃) pro analysis (p.a.) and Chloroform-D1 (CDCl₃) solvents. There are variations in the number of scans (quickscan, standarscan, and powerscan) to determine the optimum measurement conditions.

2.3. Preparation of standard curve with the addition of internal standard
The surfactant solution is made with several concentrations of 0.1%; 0.2%; 0.3%; 0.4% and 0.5% w/w using water injection. Then the surfactant solution was extracted using the SPE technique at optimum conditions. The extracted sample was then measured using Benchtop $\textsuperscript{1}H$ NMR 43 MHz with the addition of an internal standard solution (DMF or Toluene).

2.4. Measurement results of core flooding using SPE and measurement techniques $\textsuperscript{1}H$ NMR

Results surfactant solution which has passed through the reservoir rock cores using the technique of flood, the surfactant concentration tested using the simultaneous quantification with $\textsuperscript{1}H$ NMR. The core flooding samples were extracted using SPE tube (d= 0.72 cm), Silica C-18 stationary phase (m = 1.85 g, t = 1.5 cm) with MeOH (1mL) eluent, EtOAc (4 mL), and n-Hexane (4 mL). Furthermore, the extracted sample measured $\textsuperscript{1}H$ NMR 43 MHz in CDCl$_3$ (400 µL) solvents with a standard internal addition of DMF (0.5% w/w 20 µL).

3. Results and discussion

3.1. Optimization of Solid Phase Extraction (SPE) techniques for nonionic surfactants

The SPE technique is influenced by two important factors, namely the type of stationary phase and the mobile phase (Eluent) used. Selection of stationary phase very dependent on the type of compound and sample dissolved in organic solvents or water. In this case, the type of surfactant compound to be analyzed is a group of nonionic compounds with polar groups derived from poly-oxo compounds (PEG) and nonpolar groups derived from carbon chains 18 (Oleic Acid) which are dissolved in water solvents. Based on the type of compound that is very polar in water solvents, the stationary phase with ordinary silica or silica C-18 is used.

Eluent used is conditioned to stationary phase using a solvent MeOH 1 mL, 4 mL EtOAc and Hexane 4 mL. The experimental results showed that the right type of stationary phase for extracting nonionic surfactants was using silica C-18. This is shown on TLC test results, where the results using ordinary silica SPE did not show any stain (Figure 1). In contrast to the SPE results using Silica C-18, the presence of stains on TLC proves success in surfactant extraction from the aqueous phase to the organic phase (Figure 1).

![Figure 1](image-url). Profile results of TLC chromatograms extraction with (a) Silica and (b) silica C-18, Eluen n-hexane: EtOAc (8:2).

Optimization of the SPE technique was carried out by varying the mass of silica C-18. The optimum conditions of high silica which is used for extracting the surfactant are 1.5 cm (0.35 g) as shown in Table 1.

Silica C-18 is different from the usual type of silica consisting of silicate resin and alumina resin without modification. Silica C-18 was introduced using an alkyl chain which is covalently bonded to the supporting phase, namely silica which consists of silicate resin and alumina resin. So that this type of silica can involve water as an eluent because silica is hydrophobic. To prove the measurement spectrum is from a surfactant sample not the result termination of bonding hydrolysis of the alkyl part.
of silica C-18. Then elution of the silica C-18 SPE was carried out using solvents used when working on SPE without adding surfactant samples.

**Table 1.** Comparison of mass silica C-18 to the ability to extract surfactant with a mass of 0.01 mg.

| No | Kinds of Silica | Mass (g) | Mass Sample Extraction Results (mg) |
|----|----------------|---------|------------------------------------|
| 1  | Silica C-18    | 0.17    | 0.0056                             |
| 2  | Silica C-18    | 0.35    | 0.0084                             |
| 3  | Silica C-18    | 0.43    | 0.0073                             |

If the results obtained elution peak of the aliphatic region of 0-5 ppm, the peaks indicate that the aliphatic chains covalently bonded to the silica and alumina resin bond is broken. Thus the use of Silica C-18 for this compound needs to be considered because it can interfere with the analysis.

![Proton NMR spectrum results of SPE tube elution with stationary phase using silica C-18.](image)

Observations of the $^1$H NMR spectrum from silica C-18 elution using aquades, followed by MeOH 1 mL organic solvents, EtOAc 4 mL, and n-hexane 4 mL did not show any peak in aliphatic protons ($\delta_{1H}$ 0–4 ppm) (Figure 2). This shows that during the extraction process there is no breaking of the covalent bonds of the alkyl portion of silica C-18 with silicate resin and alumina. The same thing can be seen from the $^1$H NMR spectrum from the second, third, and so on to the sixth silica C-18 elution. Thus the use of silica C-18 as a stationary phase can be continued (Figure 2).

### 3.2. Surfactant Measurement of extraction results with SPE technique

The results of extracting surfactant samples with optimum conditions were measured Benctop $^1$H NMR 43 MHz to detect surfactants using two types of solvents, namely Chloroform pro analysis (CHCl$_3$ p.a.) and Chloroform-D1 (CDCl$_3$). Based on the measurement results, the best solvent for measurement was to use Chloroform-D1 solvent with powerscan measurements for 30 minutes of measurement. Measurement of surfactant samples extracted using solvent CHCl$_3$ did not provide a spectrum with a good peak of the measurements taken from several types of scans performed. So that the analysis uses CHCl$_3$ solvents p.a. strongly not recommended.
Measurements using Chlorophome-D1 solvents get a peak spectrum that is good on powerscan measurements (Figure 3). Measuring using Chlorophome-D1 gives rise to all peaks of surfactants which consist of 3 chemical shift regions ($\delta_H$), which are bound aliphatic H on carbon in $\delta_H = 0$–2.5 ppm, Aliphatic H which binds to Oxygen atoms or electron pull groups at $\delta_H = 3$–4 ppm, and H which binds to double bonds (has sigma bonds ($\sigma$) and phi bonds ($\pi$)).

The surfactants to be analyzed are surfactants derived from palm oil with the basic framework of compounds are linear alkyl, have double bonds, and ether groups. With the result that this surfactant compound does not have a peak there is a chemical shift above 5 ppm.

**Figure 3.** Spectrum of proton NMR nonionic surfactant.

**Figure 4.** Proton NMR spectrum OGEP 0.3% surfactant uses the standard internal DMF (1%, 10µL) CDCl$_3$ 400µL.

Internal standards that can be used are Dimethyl Formamide (DMF) and Toluene based on solubility and chemical shift [19]. However, because when measuring using Chloroform-D1 solvents which have
7.2 ppm H peak so that the internal Toluene standard cannot be used. This is because the proton peak from toluene is in the area of the shift. So the internal standard used is DMF (Figure 4).

3.3. Preparation of standard curve with the addition of internal standard
The standard curve is made with a concentration range of 0.1% w/w to 0.5% w/w according to the concentration of surfactant used in EOR testing in the laboratory. The standard curve making functions to determine the concentration in the measurement of compounds that are not known to be concentrated using Benchtop $^1$H NMR 43 MHz. The standard curve is made based on the relationship between peak area (integration) to concentration. The integration value used is a comparison of integration in the area of aliphatic chemical shift ($\delta_{\text{H}} = 0$–2.5 ppm) derived from surfactants with the integration of the internal standard DMF ($\delta_{\text{H}} = 7.75$–8.75 ppm) 0.5% w/w on CDCl$_3$.

Based on the proton spectrum showed a decrease in the height of the alkene proton peak and the aliphatic region derived from surfactants at concentrations of 0.5% w/w until 0.1% w/w. While the proton peak of DMF has the same peak height at the time of measurement. Furthermore, measurements were made by comparing the aliphatic area of the surfactant with the peak DMF on each measurement [11]. Measuring the area is done by combining all the spectrums in the form of Whitewash Stacked and then equalizing the height of the part of the DMF peak at 8.0 ppm chemical shift so that the merging peak is obtained as shown in Figure 5.

After obtaining peak height matching for DMF at each peak, the next step is to determine the integration of each peak to create a standard curve. The integration will be seen in the state of incorporation in the form of a superimposed spectrum (Figure 5.b).

![Figure 5. The combined spectrum proton NMR of surfactant concentration variation (0.1%; 0.2%; 0.3%; 0.4%; and 0.5%) using standard internal DMF (1%, 10µL) CDCl$_3$ 400µL in (a) Whitewash Stacked (b) Superimposed.](image)

Furthermore, after obtaining the suitability of the data, a standard curve is made from the aliphatic part of the constituent framework of the surfactant. Based on the calibration curve made with several variations of measurements, the equation of the line obtained with the value $R^2 = 0.992$. With a value of $R^2 > 0.9$ [9], this standard curve can be used in the analysis of determining the surfactant concentration with a range of 0–0.5% w/w (Figure 6).
3.4. Measurement results of core flooding using SPE and measurement techniques $^1$H NMR

The results of core flooding surfactant with a concentration of 0.3% b/b were collected as many as 19 vials (Vial number 2-20) and 1 vial control (Vial number 1). Then each vial was extracted using SPE and $^1$H NMR measurements. The measurement results showed the presence of surfactants began to be detected in the 7th vial to 18th vial. Vials with the largest surfactant concentration were detected in the 13th to 16th vials.

![Figure 6. Calibration Curve based on integration versus concentration.](image)

![Figure 7. Surfactant concentration curve from core flooding.](image)

Based on this research, it can be seen that the concentration determination technique using $^1$H NMR and SPE can be used for compounds that do not have chromophore groups or colourless solutions. For example, nonionic surfactants were determined as concentrations for kinetic adsorption test analysis. The concentration of each vial resulting from surfactant injection using a flooding tool can be measured using this technique.
4. Conclusion
The optimum conditions for extracting nonionic surfactant OGEP (Oleil Glycerine Ether-Polyethylene Glycol) can be done using the Solid Phase Extraction (SPE) technique with silica C-18 stationary phase (tube diameter =0.72 cm; high in silica=1.5 cm) using MeOH, EtOAc, and n-Hexane (1 mL, 4 mL, and 4 mL). The extraction results were measured by $^1$H NMR instruments using CDCl$_3$ (400 µL) solvents and DMF internal standard (0.5% w/w, 20 µL) for concentration determination.

Acknowledgments
This paper is the collaboration results of Research Centre for Oil and Gas Technology “LEMIGAS” and Organic Synthesis Laboratory of Chemistry, Bandung Institute of Technology. Special thanks to Dr. Untung Triadi, M.Si for sharing about SPE techniques. The financial support from DIPA Research Center for Oil and Gas Technology “LEMIGAS” is fully acknowledged.

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