



Preparation and Evaluation of 1, 2-Dibromoethane Product as Oil Field Emulsion Breaker

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

Article Information

DOI: 10.9734/AJACR/2022/v12i2218

Open Peer Review History:

This journal follows the Advanced Open Peer Review policy. Identity of the Reviewers, Editor(s) and additional Reviewers, peer review comments, different versions of the manuscript, comments of the editors, etc are available here: <https://www.sdiarticle5.com/review-history/93788>

Original Research Article

Received: 09/09/2022

Accepted: 15/11/2022

Published: 25/11/2022

ABSTRACT

Quercetin rich compound and cardanol rich compound were extracted and modified via the William ether synthesis using 1,2-dibromoethane in the presence of a base catalyst. The FTIR spectral analysis of the modified product confirmed its chemical modification. The modified product MRCNSL was evaluated as emulsion breakers. Medium crude and seawater, characterized with ASTM standards were used in producing laboratory-simulated crude oil emulsions at varying crude oil: water mixing ratios of 90:10, 70:30 and 50:50. Performance of MRCNSL demulsifier was evaluated based on variation in dosage (10 ppm – 50 ppm), water content (10%, 30% and 50%), and solvent types (ethanol, butanol, xylene and a binary mixture of butanol and xylene in ratio 30:70, 50:50 and 70:30) at room temperature within a 3-hr period via bottle testing. Results obtained showed that water separation increases with demulsifier concentration and emulsion water content respectively, though water separation varied among the solvents. In conclusion, the

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evaluated MRCNSL product possesses emulsion breaking potential using binary mixture of Butanol/xylene (70:30) as solvent at shorter times. This may be due to the synergetic effect of Butanol as a solvent, thus, Butanol/xylene (70:30) should be considered as solvent substitute for xylene due to reduced cost and less toxicity levels, unlike using xylene alone which is toxic and expensive.

Keywords: Emulsion; emulsifier; demulsifier; flavanoids; crude oil; modification; characterization.

1. INTRODUCTION

A major problem in industrial applications, such as the petroleum industry, is the production of water in oil emulsion. In fact, emulsified water can corrode refinery machinery, and downstream processing facilities' catalysts can get poisoned by the salt that is dissolved in the water. [1]. Additionally, water in oil emulsions frequently display viscosities that are noticeably higher than crude oil. The cost of pumping oil through pipelines will rise as a result of this. Oil and water typically cannot mix. The inclusion of a surfactant throughout the refining process increases their miscibility [2].

The breaking of crude oil emulsion is a crucial step in the processing of crude oil. Chemical demulsification is the most often used technique for separating the water from an oil emulsion. Demulsifiers made of chemicals harm the environment.

Demulsification is required since crude oil is extracted as an emulsion. As mentioned above, the production facilities may have issues due to the emulsion's water concentration.

Demulsification can be done in a variety of ways, including chemically, mechanically, and

thermally. The chemical demulsifiers, which are often used and have been shown to include methyl benzene, have a negative impact on the environment [3]. After additional processing, the emulsion's extracted water will be released into the environment, and it has been discovered that this water is poisonous and harmful for marine life. For this reason, there is a need for green demulsifiers.

1.1 The Theory of Emulsion

An emulsion is a nanocrystalline dispersion of two immiscible liquids, such as oil and water, in which one of the liquids is dispersed in the other [4]. Emulsions can be simple or complex. Simple emulsion systems can be divided into two categories, namely:

- Oil-in-water (O/W) emulsions: In this type of emulsion, oil is dispersed in a continuous water phase. The dispersed phase is the oil while the continuous phase is water.
- Water-in-oil (W/O) emulsions: In W/O emulsion, water is the dispersed phase which is dispersed in an oil continuous phase [5].

The diagrammatic representation of simple emulsion is shown in Fig. 1.

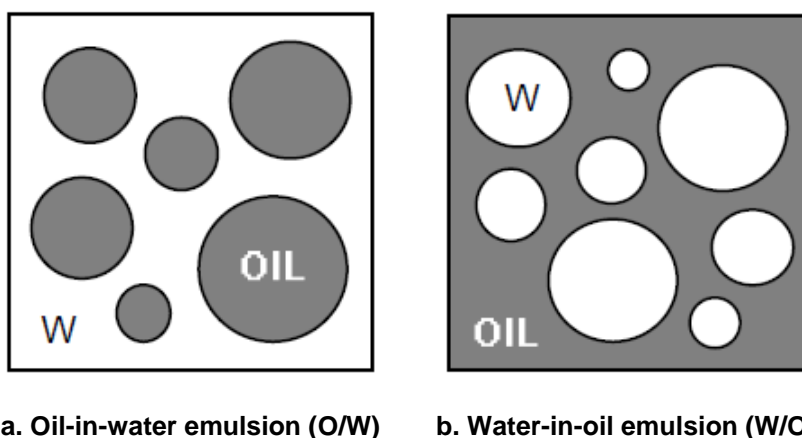


Fig. 1. Diagrammatic representation of simple emulsions

Multiple emulsions are more complex systems. In this system, the dispersed phase is itself an emulsion. This can also be classified into two major types:

- a. Oil-water-oil (O/W/O) emulsions: oil-water emulsion is the dispersed phase dispersed in oil which is the continuous phase [5].
- b. Water-oil-water (W/O/W) emulsions: here the dispersed phase is a water-in-oil emulsion dispersed in water which is the continuous phase.

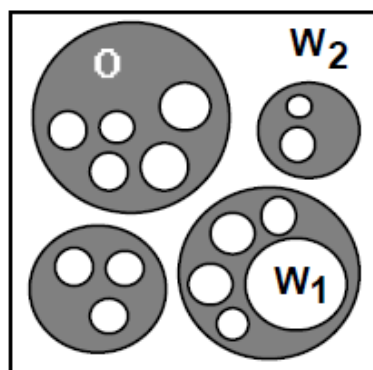
The diagrammatic representation of multiple emulsions is shown in Fig. 2.

W/O/W emulsion can be created by one step emulsification or two step emulsification, respectively. Phase inversion and intense mechanical agitation are examples of one-step emulsification techniques. A W/O emulsion originally forms, but a portion of it inverts and creates a W/O/W emulsion. Making a fine

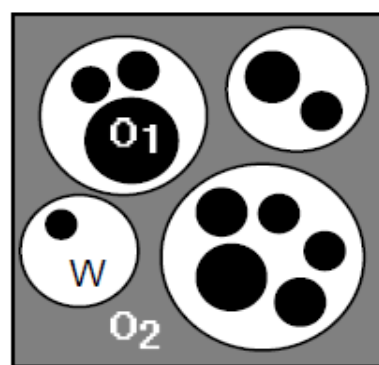
primary W/O emulsion in two steps involves using a hydrophilic emulsifier to disperse the primary emulsion in a solution [6]. The inherent stability of the emulsion created is a crucial aspect in determining how effective this procedure is.

Emulsions can be of advantage and of disadvantage. Table 1 shows the different emulsions that can be considered advantage or desirable and the disadvantaged which is undesirable.

Water-in-oil emulsions are stabilized by a wide range of materials that appear naturally in the heavy crude oil, such as asphaltenes (Bio-based surfactants) and clays. To resolve water from the emulsion to meet the pipeline and shipping specifications, the destabilization of emulsion is essential. The destabilization mechanism of water in oil emulsion during demulsification is shown in Fig. 3.



a. Oil-water-oil emulsion (O/W/O)



b. Water-oil-water emulsion (W/O/W)

Fig. 2. Diagrammatic representation of multiple emulsions

Table 1. Desirable and undesirable emulsion

Emulsion Description	Type of emulsion	Desirable	Undesirable
Heavy oil pipeline emulsions	O/W	√	
Oil floatation process emulsion	O/W	√	
Emulsion drilling fluid: oil-emulsion mud	O/W	√	
Oil-base mud	W/O	√	
Asphalt emulsion	O/W	√	
Enhance oil recovery from in situ emulsions	O/W	√	
Fuel oil emulsion (70% heavy oil)	O/W	√	
Wellhead emulsions	W/O		√
Fuel oil emulsions	W/O		√
Oil floatation process froth emulsion	W/O or O/W		√
Oil floatation process dilution froth emulsion	O/W/O		√
Oil spill mouse emulsions	W/O		√

Source: Schramm, [54]

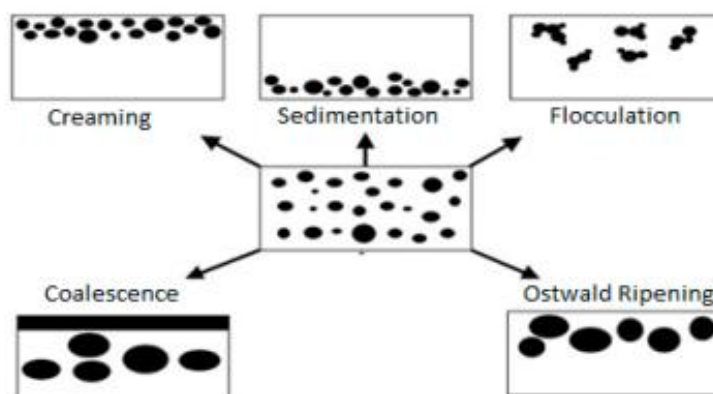


Fig. 3. Destabilizing mechanisms of emulsions during demulsification

1.2 Crude Oil Demulsification

“Demulsification (emulsion breaking) is needed in many practical applications such as petroleum industry, environment technology, and wastewater treatment. Demulsification is the process of separating water from crude oil. Crude oil need to be separated efficiently and quickly from the water to allow further treatment. The purpose of this is to maximize crude oil value and minimize operating cost” [7].

“Chemical demulsification is the most widely used method currently and in the past few decades. The chemical structure of these demulsifiers is usually based on alkylphenol formaldehyde ethoxylated resins. These chemical demulsifiers are effective, but, unfortunately, they are believed to be endocrine disrupters, and thus it is likely that they may be banned by various national environmental protection agencies” [7].

1.3 Demulsifiers

“Demulsifiers are molecules that aid the separation of oil from water usually at low concentrations. They prevent formation of water and oil mixtures. Demulsifiers typically have limited solubility in the oil phase and migrate to the oil/water interface when the oil is mixed with water. Demulsifiers are surfactants that are important in breaking the emulsion system” [8]. The presence of demulsifiers accelerates the flocculation of water droplets and enhances the film drainage before its rupture. A good demulsifier will be able to decrease the surface elasticity of the interfacial film and must have a high diffusivity.

1.4 Classification of Demulsifiers

“There are four types of demulsifiers that are used to break the crude oil emulsion. They are anionic, cationic, nonionic, and amphoteric. Early demulsification relied on the reversal of the emulsion type demulsifier such as hydrophilic ionic demulsifiers. These types were followed by oil-compatible nonionic surfactants based on ethylene and propylene oxide resins” [9]. “The most effective demulsifier formulations are achieved from the combination of all four types of demulsifiers. The classification given is based on the chemical structure of the hydrophilic group” [10].

“Anionics are used in practically every type of detergents, which are the main application of demulsifiers. This is because they are easy to produce and have low manufacturing cost. Anionics are manufactured and used in greater volume compared to all other types of demulsifiers” [10]. “The surface-active part of the anionic molecules carries a negative charge and has a long-chain hydrophobe carrying the negative charge. The anionics have the advantage of being highly stable foaming agents; however, they do have the disadvantage of being sensitive to minerals and the presence of minerals in water (water hardness) or pH changes” [10].

“Nonionic demulsifiers are demulsifiers that do not contain a charged group. Nonionic surface active agents have a hydrophobic-hydrophilic balance wherein there is neither a negative nor a positive charge in either part of the molecule, thus giving it the nonionic terminology. These surface-active agents have the advantage that they are not affected by water hardness or pH

changes as the anionic and cationic demulsifiers are, and in many cases it is an advantage that they are considered medium to low foaming agents. It is especially advantageous when a very low-foaming surface-active agent is required. A water soluble group that does not ionize to any great degree provides the hydrophilic group" [10]. "Those groups used in practice are shown in Table 2. Sometimes mixtures of nonionic, cationic, or anionic materials are used together, depending on the oil characteristics. Ethoxylated nonionic surfactants are effective, multi-purpose, and versatile substances. Commercial products are obtained by reaction of ethylene oxide with a hydroprobe having an active hydrogen group (e.g., fatty acids, alkylphenols, or fatty alcohols) in the presence of suitable catalysts. Sjoblom et al. stated that a similar destabilization sequence for model and authentic crude oil emulsions can be obtained when medium-chain alcohols and fatty amines are used as destabilizers. The commercial demulsifiers that are used to break up water-in-oil emulsion are oil soluble and water-soluble demulsifiers" [11]. Table 2 shows the comparison between those demulsifiers.

"Amphiphilic block copolymers contain hydrophilic poly ethylene oxide (PEO), and hydrophobic poly propylene oxide (PPO) blocks are commercially available and widely used" [12,9]. "Variation of the molecular characteristics (PPO-PEO composition ratio by molecular weight) of the copolymer during the synthesis allows the production of molecules with optimum properties that meet the specific requirements of different applications" [13-15]. "As a result, PEO-PPO-PEO block copolymers find widespread industrial applications in detergency, dispersion stabilization, foaming lubrication, and demulsification" [16,17]. "Interfacial properties

and aggregation behaviors of PEO-PPO-PEO aqueous solutions, including the surface tension, critical-micelle concentration, and aggregation conformation, often play a control role in determining and controlling copolymer performance in many practical applications" [18-21]. "Commercial demulsifiers are polymeric surfactants such as copolymers of polyoxyethylene and propylene or alkylphenol-formaldehyde resins or blends of different surfactant substances. PEO-PPO-PEO block copolymers can be used as demulsifiers. These demulsifiers are surface-active agents and develop high surface pressures at the crude oil-water interface. This results in the replacement of rigid films of natural crude oil substances by a film which is conducive to coalescence of water droplets" [22-24,18]. "Therefore, the demulsification mechanism of demulsifiers is quite complicated, and no single demulsifier can be applied to break all kinds of crude oil emulsions" [25], (Sjoblom et al. 1990) and [26].

1.5 Demulsification Mechanism

"The mechanism of demulsification and the principal role of the surfactant in destabilization of emulsion have been studied by many researchers" [27-30]. "Demulsification is believed to be accompanied by inversion followed by coagulation. It is important to note that the coagulation of the dispersed phase occurs as a two-stage process namely flocculation and coalescence. In the second stage, termed coalescence, aggregates combine to form a single drop (cluster)" [31]. This is an irreversible process, leading to a decrease in the number of water droplets and finally to complete demulsification.

Table 2. Water soluble group

Group name	Functional group	Properties
Hydroxyl	C-OH	Poor hydrophilic properties
Ether	C-O-C	Poor hydrophilic properties
Amine oxide	N-O	Excellent hydrophilic properties
Phosphine oxide	P-O	Excellent hydrophilic properties
Sulphoxide	S-O	Excellent hydrophilic properties
Triple unsaturation	C≡C	Very Poor hydrophilic properties
Ester group	COO-	Very Poor hydrophilic properties
Amide group	CO-NH ₂	Very Poor hydrophilic properties

1.6 Factors Affecting Demulsification Efficiency

There are several factors affecting the efficiency of a demulsifier. A number of them are explained thus:

1.6.1 Effect of the chemical structure

Chemical demulsification is an important method of treating W/O emulsions [32]. In which chemicals (surfactants) are added to the emulsions. The chemical structure of the effective demulsifiers mainly contains a hydrophobic backbone in addition to the more hydrophilic head group side chain. The hydrophobic segments, which are oil-soluble, can then match the asphaltenic fraction of the crude oil, thus enhancing the demulsification efficiency.

1.6.2 Effect of water content

“Water content in water in oil emulsion is one of the important factors effecting demulsification efficiency or the stability of an emulsion in general. Tough emulsions are not only dependant on asphaltene, resin, and paraffin content but also on water content. However, at low water content, the external pressure of the continuous phase (oil) is greater than the internal pressure of water droplets” [33]. “This leads to an increase in the mechanical stability of the interface film such that breaking of this strong interface film will need a high temperature and strong demulsifier. On the other hand, at increasing water content, the external pressure of the water phase becomes less than the internal pressure” [34]. This leads to an increase in the interface film thinning, so that the drawing of water droplets will be increased. In a regular water in oil emulsion, the maximum stability of an emulsion will occur at a set ratio of water to oil. Typically, this maximum is found at low water content as water droplets have a small chance of colliding and coalescing with each other. Increasing the water percentage may be destroying the stability of an emulsion.

1.6.3 Effect of demulsifiers concentration

“The concentration of demulsifier required to disrupt an oil/water interracial film depends on the extent of film compression, which increases with the age of the oil-water interface” [35]. “In aged emulsions, higher demulsifier concentrations are required to cause destabilization. However, since most demulsifiers

are also emulsifiers, the emulsion may invert if excess amounts of demulsifier are added” [36].

In order to solve this problem, we have utilized 1,2-dibromoethane to synthesize an innovative emulsion breaker for crude oil in water emulsion, which can achieve demulsification economically and environmentally friendly. Flavonoid derivatives (red onion skin extract and Cashew nut shell liquid) will be used in conjunction with 1,2-dibromoethane as a green demulsifier.

1.7 Flavonoids

A subclass of polyphenols known as flavonoids has many different characteristics. There are variations in the location, structure, and synthesis of the over 3000 different flavonoids. Many plant tissues, including flowers, fruit, leaves, heartwood, and bark, contain flavonoids. The flavan rings are labeled A, C, and B, with a systematic numbering of carbon atoms, as seen in Fig. 4. [37].

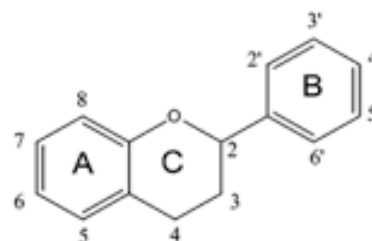


Fig. 4. Flavan unit

A significant class of naturally occurring polyphenols known as flavonoids is present in a wide range of plant-based foods [38,39]. A significant source of carbon produced from plants in the environment is flavonoid compounds. Tannins get into the soil through plant degradation and precipitation [40]. The anti-inflammatory, anti-cancer, anti-microbial, anti-fungal, and cardio protecting properties of flavonoids are well established. These processes have been connected to flavonoids' antioxidant capacity, which is correlated with their hydroxyl group content [39].

Fruits and vegetables' colors are also a result of flavonoids. A plant pigment known as quercetin belongs to the flavonoid family. From the red onion skin, it will be removed and used to create demulsifiers. Additionally, a liquid derivative of cashew nuts will be used.

1.8 Red Onion Skin

Red onions are a plant variant of the onion (*Allium cepa*), sometimes known as purple onions in some European nations. They feature reddish-purple skin and white meat. The *Allium cepa* L. onion is a member of the Liliaceae family, usually referred to as the lily family. Everywhere in the world grows it. They are the second-most popular horticultural vegetable, behind tomatoes (bulb vegetable to be precise) [41]. Each step in the preparation and processing of onions is characterized by wastes and byproducts with potential environmental effects. Approximately 450,000 tons of onion trashes are produced each year in the European Union [42].

The red skin, the outer two fleshy leaves, and the top and bottom bulbs are the main by-products of the industrial peeling of onion bulbs. One of the most valuable sources of natural dye is red onion skin [41]. It has a high concentration of dietary flavonoids [43]. Compared to the fleshy bulb, these chemicals are more concentrated in the onion skin [44]; (Yao et al., 2004); Sellappan and Akoh, [42].

In addition to improving our understanding of their biological functions, the extraction and identification of flavonoids from onion skin might also create a theoretical foundation for the use of these substances in other types of study.

Over the past ten years, major efforts have been made to characterize red onions and the

flavonoids found in their skin [45,46], which has greatly improved our understanding of these substances. The systematic isolation and identification of flavonoids from red onion skin is still poorly understood despite these investigations. In Fig. 5, the onion bulb and its cross section are shown.

1.9 Cashew Nut Shell

In Nigeria, cashew is widely farmed, primarily for its kernel. The shell is typically seen as waste [47]. A by-product of the cashew nut industry, cashew nut shell liquid (CNSL) is extracted from the spongy mesocarp of the cashew nut (*Anacardium occidentale* L.) shell using a number of methods, the most popular of which being solvent extraction [48]. It is incredibly rich in phenolic lipids such as anacardic acid, cardol, cardanol, and 2-methyl cardol.

An agricultural by-product of cashew nut production known as cashew nut shell liquid is recognized as a useful and significant raw resource for the synthesis of polymers. It is recognized as a versatile and significant raw material for the synthesis of polymers and is one of the main commercial sources of naturally occurring phenols [49]. In addition to being affordable and renewable, cashew nut shell liquid can successfully replace phenol. It is a dark-brown viscous oil with a distinctive scent, unlike other vegetable oils [50]. The cashew fruit and its cross section is shown in Fig. 6.



Fig. 5. Red onion bulb and its cross section

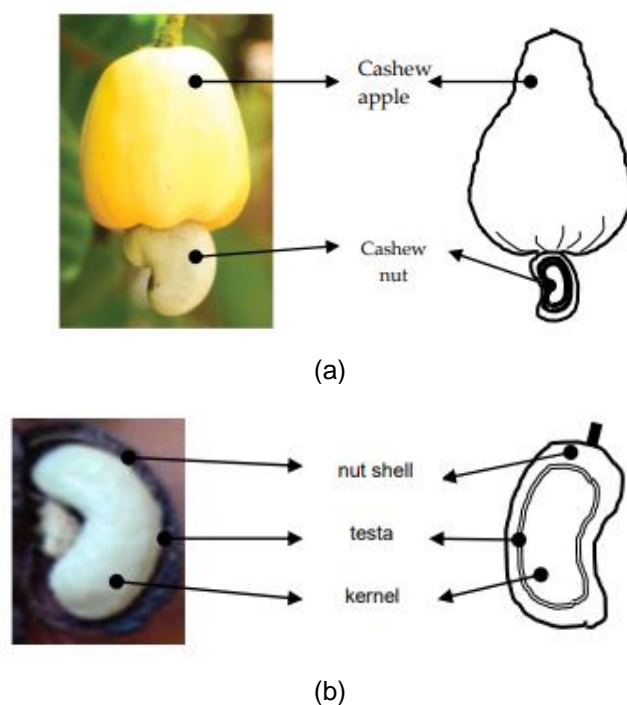


Fig. 6. (a) Cashew fruit (b) Cashew nut and its cross section

2. MATERIALS AND METHODS

2.1 Materials

2.1.1 Apparatus, glass wares and equipments

The experimental instruments and materials used in this study include: whatman filter paper, aluminum foil, timer clock, glass rod, conical flask, flat bottom flask, beaker, lie big condenser, rotary evaporator, weighing balance, hot plate with magnetic stirrer.

2.1.2 Sample Collection and Preparation

Red onion skin: The red onion skin used in this study was provided by Choba Market in Port Harcourt, Rivers State. To clean it up and make it acceptable for mixing, the red onion skin was hand-picked and sun-dried for some days. A blender was used to expand the surface area of the red onion skin. The essence of expanding the surface area is to boost the rate of extraction by enhancing the interaction between the rose and the solvent.

Cashew nut shell: Whole cashew nuts (CN) were purchased from Ihube village in Imo State, Nigeria in Okigwe Local Government Area. To remove contaminants, the cashew nut was washed and sun dried for a few days before

being chopped lengthwise, dekernelled, and crushed in a hydraulic press (to increase the surface area for extraction).

Seawater: Seawater from the Gulf of Guinea was collected, labeled, and sent to the laboratory for characterization.

Crude oil: Crude oil was obtained from a flow station in the Niger Delta region, labeled, and sent to the lab for analysis.

Chemicals: Acetone, 1,2-dibromoethane, and potassium carbonate, butanol, ethanol, xylene are some of the chemicals employed (Analar grade Aldrich Chemicals). All chemicals were used as received, with no further purification.

2.2 Methodology

2.2.1 Rose extraction

The blended red onion skin was packed in a Soxhlet extractor thimble with a Whatman filter paper and extracted by refluxing acetone at 60-70°C until the solvent in the thimble became clear. To separate the extract from the solvent, distillation was used. The extract was named ROSE.

2.2.2 CNSL extraction

Three hundred grams (300 g) of crushed cashew nut shell was packed in the soxhlet extractor thimble using a Whatman filter paper and extracted by reflux with acetone at 60 to 70°C until the solvent becomes clear in the thimble. The extract was named CNSL. The CNSL was recovered from the solvent by distillation technique.

2.2.3 Preparation of green demulsifier

The flavonoids extracted were chemically changed using the Williams ether synthesis method in an etherification reaction with 1,2-dibromoethane.

2.2.4 Modification of ROSE and CNSL with 1, 2-dibromoethane

Quercetin (approx. 8.7 g, 0.029 mol) and powdered potassium carbonate (approx. 0.5 g, 0.004 mol) were dissolved in cashew nut shell liquid (10 mL). The solution was heated to reflux for 15 minutes, then cooled before adding 1,2-dibromoethane (1.2 ml). The reaction mixture was refluxed for 1 hour, then cooled, filtered, and concentrated by rotary evaporation to produce a brown liquid (Pizzi, 1983). The functional group contained in the molecule was confirmed using FTIR. The product was named MRCNSL.

2.3 Sample Characterization

2.3.1 Rose extract

Physicochemical properties:

- Color Determination: The color of the extracted sample was determined using Color charts. The color was compared to the colors on the chart. (Warra et al., 2011).
- Density: The extract's specific density was determined according to the method used by John in 2003. A weigh balance was used to determine the weight of the extract. The extract's specific density was calculated using the equation below.

$$\text{Specific density} = \frac{\text{mass of extract}}{\text{volume of extract}} \quad (1)$$

- Iodine value: 0.50 g of the extract was dissolved in carbon tetrachloride in a 100ml conical flask to determine the iodine value. 5 mL of iodine was added to the flask and left to stand for 2 hours at 25°C in the dark. The mixture was titrated with 0.1M sodium thiosulphate (Na₂S₂O₃) using starch indicator

and 5ml potassium iodide (KI) solution. The iodine value was determined using the formula below after performing a blank determination.

$$\text{Iodine value} = 12.69 \times (B-S) \times \frac{N}{W} \quad (2)$$

Where: B= titre value for blank, S = titre value for sample, N = normality of thiosulphate, W= weight of the sample.

- Determination of Free Fatty Acid: To determine free fatty acid, 0.5GA of extract in 5 cm³ ethanol was boiled, cooled and 2 drops of phenolphthalein indicator was added. The ethanol used was neutralized before analysis. The resulting solution was titrated with 0.1M NaOH until pink color disappears (AOAC, 1998).

$$\text{Free fatty acid} = \frac{28.2 \times V \times N}{W} \quad (3)$$

Where: V= Titre value, N= Molarity of acid, W= weight of sample.

- Saponification Value: 2g of the extract sample was put to a flask containing 30 cm³ ethalonic KOH, which was then attached to a condenser for 30 minutes to ensure the sample was completely dissolved. After cooling the sample, 1 cm³ phenolphthalein was added and titrated with 0.1m HCl until a pink end point was achieved. The analysis was done with a blank, which was made with the identical reagents but without the oil.

$$\text{Saponification value} = \frac{(S-B) \times M \times 56.1}{\text{sample weight (g)}} \quad (4)$$

Where: S= sample titre value, B= blank titre value, M= molarity of the HCl, 56.1= molecular weight of KOH.

- Peroxide Value: 2g of the extract was mixed with 12 cm³ chloroform and 10cm³ acetic acid in a 22 cm³ solution. The flask was filled with 0.5cm³ of saturated potassium iodide (KI). It was chilled and shaken occasionally before being titrated against 0.1M Na₂S₂O₃ until the yellow color was practically gone. 0.5 cm³ starch indicator was promptly added, and the titration was continued until the blue color was almost completely gone. At the same time, a blank titration was carried out.

$$\text{Peroxide value} = \frac{(S-B) \times M \times 1000}{W} \quad (5)$$

Where: S= volume of titrant (cm³) for sample, B= volume of titrant (cm³) for blank, M= molarity of Na₂S₂O₃ solution (in Eq/ cm³), W= weight of sample.

- Acid Value: In a 250ml beaker, 100cm³ of neutral ethyl alcohol was heated with 2g of extract sample until it boiled, then titrated with 0.1M KOH solution using two drops of phenolphthalein as an indicator and constant shaking until a persistent pink color was formed.

$$\text{Acid Value} = \text{Free fatty acid} \times 1.99 \quad (6)$$

- Refractive Index: This was determined at 20⁰C using an Abbe Refractometer (Reichert AR 700). The measurements were performed in triplicate and results were averaged.

2.3.2 Crude oil

- **Water cut**

The water-cut was determined using the Dean-Stark distillation method, as described in ASTM D4006-11. Using agitation, homogenize the sample and pour 100 mL into a round bottom flask. Fill the flask halfway with xylene, attach the dean and stark receiver traps to the condenser, and heat for one hour. Record the amount of water gathered in the trap and use the calculation below to calculate the amount of water cut:

$$\text{Water cut \%} = \frac{\text{volume of water collected in the trap}}{\text{volume of sample}} \times 100 \quad (7)$$

- **Kinematic viscosity**

The ASTM D455-12 method was used to determine kinematic viscosity at 40°C and 100°C using a Stanhope-Seta KV-8 viscometer bath. A 100 ml centrifuge tube was filled to the top with crude oil sample and centrifuged for 15 minutes at 50,000 revolutions per minute (rpm). The waterless centrifuged sample was poured into a viscometer tube that had already been corked with a stopper at the smaller aperture, attached to a viscometer tube handler, and placed in the viscometer bath. A thermometer was dipped into the sample to determine when the proper temperature (40°C or 100°C) was reached, the cork was removed, and the oil was allowed to flow. When the oil reaches the first line over the little bulb's upper neck, the timer clock starts counting down until the oil hits the line above the

big bulb. The efflux time is measured in seconds, and the kinematic viscosity is estimated in centistokes (cSt) using the formula below:

$$\text{Kinematic viscosity (cSt)} = \text{calliberation constant (c)} \times \text{Efflux time (in secs)} \quad (8)$$

- **Sulphur content**

Sulphur content of the crude was determined according to ASTM D4292-16 using a Horiba Sulphur-in-oil analyzer.

- **Specific gravity and API gravity**

Specific (60/60°F) of the sample was determined according to ASTM D1298-12b. The API gravity calculated using the equation below:

$$\text{API gravity} = \frac{141.5}{\text{specific gravity}} - 131.5 \quad (9)$$

- **Pour point**

The pour point was determined using the ASTM D5853-17a method and a Stanhope-Seta Pour Point refrigerator. In a thermostatic water bath, the crude oil was pre-heated to 45°C in the test jar before being placed in the pour point refrigerator. The test jar was gently taken out of the fridge to check for flow until the pour point was achieved. The ultimate pour point value was increased by three degrees Celsius (3°C).

- **Base, sediment and water (BS&W)**

The crude's BS&W content was determined using the centrifuge method according to ASTM D4007-11. Fifty millilitres of sample were transferred to a centrifuge tube (100 ml) and xylene was added in an equal volume. The mixture was mildly agitated 10 times in a to and fro motion with five (5) drops of demulsifier (0.5 ppm equivalent). The tube was placed in a thermostatic water bath at 60°C for 15 minutes before being centrifuged for 10 minutes and readings collected.

2.3.3 Sea water

- **Specific gravity and density**

The specific gravity and density were determined according to ASTM D1429-13 method using a hydrometer and density calculated via the specific gravity- density relationship in the equation below.

$$\text{Specific gravity} = \frac{\text{density of liquid}}{\text{density of water}} \quad (10)$$

- **Total dissolved solids (TDS)**

The ASTM D5907-18 technique was used to quantify total dissolved solids. Before weighing, the crucible was preheated to a constant weight of 180°C and placed in the desiccator for two hours. A hundred millilitres (100 ml) of saltwater sample was vacuum-filtered into a receiving flask using a 45 µ filter paper. The saltwater filtrate was added to the constant weight crucible, which was then placed in a water bath. The filtrate was allowed to dry completely before being oven dried and weighed. The equation below can be used to compute total dissolved solids.

$$\text{Total dissolved salt (ppm)} = \frac{(\text{weight of crucible+filtrate}) - (\text{weight of crucible})}{\text{volume of sample}} \times 10^6 \quad (11)$$

- **Resistivity and conductivity**

Using a YSI 3200 conductivity instrument, the electrical resistivity and conductivity were determined using the ASTM D1125-14 technique, and the electrical resistivity was computed using the equation below.

$$\text{Resistivity} = \frac{1}{\text{conductivity}} \quad (12)$$

- **Salinity**

Salinity was measured using the ASTM D4458-15 technique. A sample aliquot (0.1 mL) was placed in a 25 mL measuring cylinder and filled to the mark with distilled water, which was then transferred to an Erlenmeyer flask (50 ml). 0.25 mL potassium chromate indicator (5 percent w/v) was added and titrated to the equivalence point with 0.0140 N silver nitrate (AgNO₃) solution as titrant (which is pinkish yellow or brick red). The chloride content, Cl⁻, and salinity in mg/L were determined using the formulae below using the titrant volume

$$\text{Chloride content} = \frac{(\text{volume of silver nitrate used} - \text{blank}) \times \text{molarity} \times 35450}{\text{volume of sample}} \quad (13)$$

$$\text{Salinity} = \text{Cl}^- \times 1.8066 \quad (14)$$

- **pH**

The pH was determined according to ASTM D3875-03 using Thermo Scientific Orion Star A211 pH meter.

2.4 Sample Preparation

2.4.1 Demulsifier preparation

Five percent weight per weight (5%w/w) of the demulsifier was dissolved in 100cm³ volume equivalent of Ethanol, Butanol, Xylene and a binary mixture of butanol and xylene in different ratios (30:70, 50:50 and 70:30) respectively to give 50000 ppm stock solution. Two millilitres of stock solution (1000 ppm equivalent) was pipetted into the 100 ml volumetric flask and filled to mark with the respective solvents.

2.4.2 Crude oil emulsion preparation

Laboratory simulated water in oil emulsions was generated using the approach reported by [51,52] with little modification. The crude oil was combined at high speed for 30 minutes in a Hamilton Beach Commercial mixer, with saltwater gradually added until all phases were thoroughly homogenized. Different emulsions were created by altering the crude oil to water mixing ratios of 90:10, 70:30, and 50:50, respectively.

2.4.3 Crude oil emulsion breaking

The bottle testing method, as described by Atta et al. [51] and Al-Sabagh et al. [53] with minor variations, was utilized to break the crude oil emulsions. The efficiency of the demulsifier-in-solvent formulation in the simulated crude emulsions was evaluated using the bottle testing method. The simulated emulsions were poured into graduated 100 ml measuring cylinders covered with aluminum foil and dosed with the specified demulsifiers at 10 ppm, 20 ppm, 30 ppm, 40 ppm, and 50 ppm. For each experimental set, a blank was used. The bottle was shaken 100 times in a 'to' and 'fro' motion (to replicate natural mixing of crude oil and demulsifier in the flow station) and placed in the laboratory shelf at room temperature, with water separation monitored for the first 5 minutes and then every 10 minutes for 3 hours. The demulsifier's performance was measured in terms of water separation rate, interfacial layer quality, and water separated. The following equation was used to calculate water separation:

$$\text{Water separation \%} = \frac{\text{volume of water separated in ml}}{\text{total volume of water in the emulsion}} \times 100 \quad (15)$$

3. RESULTS AND DISCUSSION

The results for the characterization of sea water sample from the gulf of guinea are presented in

Table 3. Table 4 gives the results of the physico-chemical property of the crude oil used in this study. Physico-chemical characteristics of ROSE and CNSL are tabulated in Tables 5 and 6 respectively. The characteristics of CNSL have

been compared to literature values also in Table 6. The solubility test of ROSE, CNSL and their modified product (MRCNSL) are presented in Table 7.

Table 3. Characterization of sea water sample

Parameter	Method	Sea water sample
Total dissolved solids (ppm)	ASTM D 5907	32653
Resistivity (ohm) at 19 ^o C	ASTM D 1125	0.0181
Conductivity (μS/cm) at 19 ^o C	ASTM D 1125	55.41×10 ⁶
Density (g/ml)	ASTM D 1429	1.0189
Salinity (ppm)	ASTM D 4458	35931.2
Specific gravity	ASTM D 1429	1.0189
pH at 26 ^o C	ASTM D 3875	8.18

Table 4. Physico-chemical properties of crude oil sample

Parameter	Method	Value
Specific gravity (60/60 ^o F)	ASTM D 1298	0.9030
API gravity at 60 ^o F	ASTM D 1298	25.1999
Kinematic viscosity at 40 ^o C (c.St.)	ASTM D 455	13.7506
Kinematic viscosity at 100 ^o C (c.St.)	ASTM D 455	3.1469
Water cut %	ASTM D 4006	0.0250
Sulphur content (wt%)	ASTM D 4292	0.3082
Base, sediment and water	ASTM D 4007	0.025
Pour point (^o C)	ASTM D 5853	-30

Table 5. Physico-chemical characteristics of ROSE

Parameters	Values
Colour	Brown
Physical state at room temperature	Solid
Percentage yield (%)	30.2
Specific gravity (g/cm ³)	0.86
Saponification value (mg KOH/g)	211.54
Iodine value (gI ₂ /100g)	98.13
Acid value (mg KOH/g)	5.13
Peroxide value meq H ₂ O ₂	2.75
Refractive index	1.46
Free fatty acid	6.93

Table 6. Comparison of physico-chemical properties of extracted CNSL with literature

Property	Literature value		
	Research value	Idah et al. [50]	Eke et al. (2019)
Colour	Dark brown	Dark brown	Dark brown
pH	4.06	6.28	5.0
Specific gravity (22.5 ^o C)	0.870	0.903	0.984
Density (g/ml)	0.870	0.903	0.984
Acid value (mg KOH/g)	1.63	1.94	113.30
Iodine value	71.76	177.7	110.4
Yield	35%	28.85%	35.5%
Saponification value (mg KOH/g)	173.44	161	-

Table 7. Solubility test of ROSE, CNSL and their modified derivative at 25^oC

Compound	Solvent			
	Water	Ethanol	Butanol	Xylene
ROSE	Insoluble	Soluble	Soluble	Soluble
CNSL	Insoluble	Soluble	Soluble	Soluble
MRCNSL	Insoluble	Soluble	Soluble	Soluble

Table 3 shows the result of the characterization of the sea water sample. The table shows that the property of the sea water sample compared favorably with a typical sea water property. The pH value of 8.18 obtained showed that the sea water is not acidic. A sample is considered to be acidic if the pH is below 7.0. Meanwhile, it is alkaline if the pH is higher than 7.0. Acidic water can lead to corrosion of metal pipes and plumbing system. Meanwhile, alkaline water shows disinfection in water. The normal drinking water pH range mentioned in WHO and NDWQS guidelines is between 6.5 and 8.5. Prior to the Industrial Revolution, average ocean pH was about 8.2. Comparing to the pH of the sea water sample used, 8.18 is within the range. The pH of the seawater sample is mildly acidic. However a salinity value of 35931.2 ppm indicates that the sample is highly saline which a common characteristic of sea water is. Similarly, the very high conductivity value of $55.41 \times 10^6 \mu\text{S/cm}$ further confirms the property of sea water. Likewise the high value of dissolved solids still shows the characteristics of sea water.

Table 4 shows the result for the characterization of crude oil. The crude oil was sampled from an identified water free oil-well, having little or no water content and of export quality (water content of less than 0.5%), which was established by water cut and BS%W value of 0.025% respectively thus making it fit for use in the stimulation of crude oil emulsions [51-53]. They have been classified as medium heavy (according to API classification of oils between 22.3^o API and 31.1^o API) and sweet (oils with sulphur content less than 1%) crude oil. The kinematics viscosity values of 13.64 cSt and 3.15 cSt at 40^oC and 100^oC respectively which suggests that the crude oil is very viscous, and low pour point value of -50^oC suggests low paraffin content.

Table 5 shows the physic-chemical properties of the red onion skin extract. The table shows that the extract is a brown solid at room temperature. The specific gravity is less than 1; this shows that

its density is less than that of water so it will float on water. According to literature, saponification number ranges from 187.3 to 199.0. From the result, the saponification value is slightly above the standard. Iodine value is 90.0–104.8, specific gravity is 0.876–0.932, and the refractive index is 1.464–1.480 (Alpaslan and Hayta, 2006). The result also shows that the iodine value and refractive index falls within the range.

Table 6 contains the result of the physico-chemical properties of Cashew nut shell liquid as well as the literature values. The result showed that the sample is a brown liquid with pH of 4.06 which indicates acidity. The specific gravity is less than 1 while the saponification value falls below the standard range as well as the iodine value. The percentage yield was poor indicating that the method of extraction was not quite effective. Comparing the values obtained with literature, there is little or no difference.

Table 7 shows the solubility test. The result confirms that the solubility of the modified product is not different from the extracts.

The FTIR spectra of MRCNSL contain typical peaks corresponding to the functional group in quercetin and carnadol, as shown in Fig. 7. The O-H vibration of the phenol group coincides with that of carboxylic acid, resulting in a strong and broad absorption band at 3387 cm^{-1} . The disappearance of the band at 1699.7 cm^{-1} indicates that the acid group is involved in the creation of ester bonds. Other absorption bands seen at 3011.7 cm^{-1} , indicates the presence of phenol group's O-H vibration while the C-H stretching vibration of alkene groups occurs at 2922.2 cm^{-1} and the C-H vibrations of methylene and methyl groups of the meta substituted hydrocarbon chain occur at 2855.1 cm^{-1} . The band at 1510 cm^{-1} shows the alkene C=C stretching vibrations, while aromatic C=C vibrations occur at 1458 cm^{-1} . At 1365 cm^{-1} , methyl C-H deformation vibrations occur while the band at 724 cm^{-1} corresponds to alkene C-H deformation vibration.

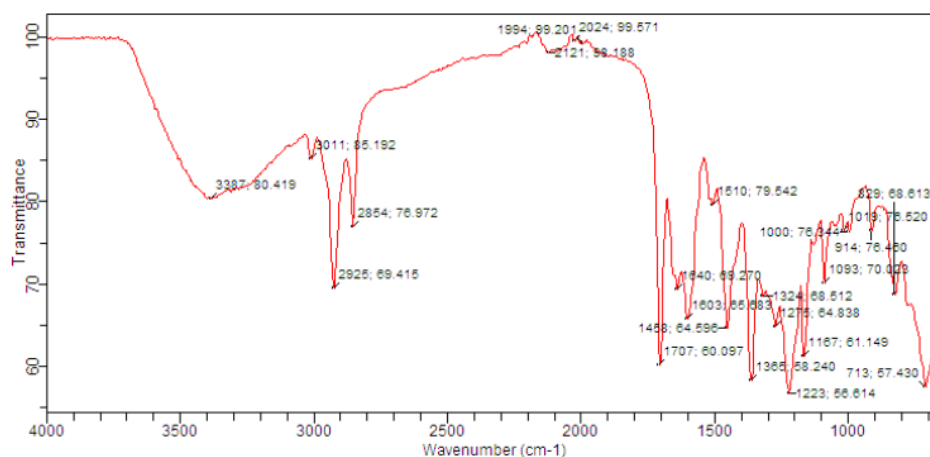


Fig. 7. FTIR Spectrum of MRCNSL

Table 8. Demulsification performance of MRCNSL in different solvents, concentration and water content

Solvent	Concentration (ppm)	10% water content		30% water content		50% water content	
		Time (secs)	% of water separated	Time (secs)	% of water separated	Time (secs)	% of water separated
Ethanol	10	6.9	180	21	180	40	180
	20	7.6	180	23	180	42	180
	30	8.8	180	25	180	48	180
	40	11	180	27	180	50	180
	50	13	180	30	180	52	180
Butanol	10	7.5	180	25	180	43	180
	20	9	180	26	180	45	180
	30	10	180	28	180	50	180
	40	13.8	180	30	180	52	180
	50	15	180	33	180	55	180
Xylene	10	4.8	180	18	180	35	180
	20	5	180	20	170	38	170
	30	5.8	180	20	180	45	170
	40	8	180	24	180	45	160
	50	11	180	25	170	50	180
Butanol/xylene 30:70	10	9.3	180	27	180	46	180
	20	11	180	28	180	46	180
	30	12	180	30	180	52	180
	40	14	180	38	180	54	180
	50	17	180	37	180	58	180
Butanol/xylene 50:50	10	9.3	180	27	180	49	180
	20	12	180	30	180	47	180
	30	13.8	180	33	180	55	180
	40	9	180	25	180	42	180
	50	18	180	39	180	60	180
Butanol/xylene 70:30	10	10.8	180	30	180	50	180
	20	13	180	33	180	50	180
	30	15	180	35	180	58	180
	40	18	180	40	180	59	180
	50	19	180	42	180	100	180

3.1 Performance Evaluation of Formulated Demulsifier in Solvents Used

The demulsifier formulated was assigned compound code MRCNSL product. It was evaluated for its emulsion breaking potentials and efficiency in ethanol, butanol, xylene and binary mixture of butanol and xylene in different ratios (30:70, 50:50 and 70:30) using laboratory simulated crude oil emulsions at varying crude oil: water ratios of 90:10, 70:30 and 50:50, and different concentrations of 10 ppm, 20 ppm, 30 ppm, 40 ppm, and 50 ppm, at room temperature. The bottle testing data for water separation in ethanol, butanol, xylene and binary mixture of butanol and xylene in different ratios (30:70, 50:50 and 70:30) are shown in Table 8. Some factors which influence emulsion breaking were studied and are discussed as follows:

3.2 Effect of Concentration

Several sets of experiments were done to evaluate the effect of concentration on water separation, as this parameter governs adsorption of demulsifiers at the interface. The results are presented in Table 8 above for the formulated emulsion breaker. Different solvents were used at different water content and concentrations of 10- 50 ppm at room temperature. The result revealed that increasing demulsifier concentration, increases water separation for the formulated emulsion breaker thereby reducing the time taken for demulsification to occur. This increase is clearly seen in butanol and the binary mixture of butanol and xylene. However, in xylene and ethanol marginal difference is observed as the concentration of the emulsion breaker is increased. This decrease in separation time may be due to increased partitioning which further increases adsorption of demulsifier molecules at the emulsion interface (Al-Sabagh, 2002). This can also be due to differences in the chemical structures of the solvent used. Generally, for the studied demulsifier formulation, as demulsifier concentration increases, the percentage of water separation increases [53].

3.3 Effect of Water Content

“Emulsion water content plays an imperative role on demulsifier performance. Varying proportions of crude oil: water mixing ratios, 90:10, 70:30 and 50:50, to produce different degrees of water in oil emulsions were used to investigate this parameter. By inspection of data illustrations in Table 8, water separation rates for formulated

demulsifier increased with increase in water content. This is because water drop separation becomes very difficult at low water content, because external pressure of the oil is greater than the internal pressure of the water droplets leading to increased interfacial film firmness, making it difficult for coalescence of water droplets to occur. At increased water content, the external pressure of the water droplets is less the internal pressure of the oil, leading to increased interfacial film thinning thus enhancing coalescence” (Atta et al. 2012), [53], (Al-Sabagh et al. 2007).

3.4 Effect of Chemical Structure

“Chemical demulsification method, involves the use of chemicals (mostly surfactants) to treat emulsions. Studies have shown that these surface-active agents can be produced through various methods; changing acceptor ratio, quantity and arrangement of water-loving and oil loving groups” (Al-Sabagh et al., 2016), [51]. “Chemical structures of most effective emulsion breakers contain a hydrophobic backbone and a more hydrophilic head-group side chain. The hydrophobic ends match natural emulsifiers in the emulsion (asphaltenes) thus enhancing demulsification efficiency. The table for demulsification performance shows that water separation increases with increasing water content, concentration and varies from one solvent to the other, due to differences which exist in their structures, which is of great importance in the adsorption of the demulsifier molecule on the emulsion interface” (Al-Sabagh et al. 2017). However, water separation is improved with the binary mixture of butanol and xylene in 70:30 ratio using the formulated demulsifier.

3.5 Effect of Solvent

“To investigate the effect of solvents on the demulsification efficiency; the demulsifiers were used in six solvents. The data obtained were compared and it showed that water separation for the formulated demulsifier was poor in xylene as it took longer times for little or no separation to occur, as seen in Table 8. However, comparing butanol to ethanol, water separation rate is increased as it took lesser time to achieve water separation, indicating that Butanol is a better solvent in optimizing water separation in comparison to ethanol. Butanol has a number of notable qualities that make it a suitable alternative fuel. Its energy content is 30% more than ethanol” (Qureshi and Ezeji, 2008). Solvent

adsorption weakens and ruptures the interfacial film making coalescence rapid and leading to increased water separation attributed to the synergetic (common ion) effect of the -OH group in butanol. With Butanol, water separation was achieved in shorter times compared to xylene. As stated by Ramey, butanol can be mixed with other organic compounds in any proportion or be used as the sole fuel component (100% butanol) in unmodified car engines (Ramey, 2007). Butanol was mixed in different proportion with xylene as solvents for demulsifier formulation. The result also showed that optimum performance was seen in MRCNSL using the binary mixture of butanol and xylene in 70:30 ratio having butanol in higher proportion. Interfacial quality of the emulsions was examined and water in oil interface was cloudy for bottle tests using the formulated demulsifier in xylene, while for Butanol, ethanol and the binary mixture of butanol and xylene the water in oil interface was distinct and the water phase was very clear.

4. SUMMARY

A Quercetin rich component and cardanol rich compound have been extracted from red onion skin and cashew nut shell respectively. These extracts have been reacted with 1,2-dibromoethane in the presence of a base using the Williams Ether Synthesis to modify them chemically. This change has been confirmed using the FTIR. The demulsification potential of the formulated demulsifier was evaluated using laboratory stimulated water in oil emulsions of 10%, 30% and 50% of sea water and 10ppm-50ppm of demulsifier concentration at room temperature in ethanol, butanol, xylene and binary mixture of butanol and xylene in ratio 30:70, 50:50 and 70:30. Results showed that optimum separation was achieved in the binary mixture of butanol and xylene in ratio 70:30. In summary, the goal of this study was to chemically change polyphenols in order to develop value-added products or materials that may be used in other synthetic applications especially in the demulsification process. According to a study of the literature, esterification and etherification are plausible ways to derivatize polyphenols like tannins. The Williams ether synthesis yielded a good flavonoid derivative.

5. CONCLUSION

From the experimental analysis, the following deductions can be made:

1. For the preparation of flavonoid derivatives, the method of preparation worked perfectly.
2. Etherification of polyphenols was a new way to change their chemical and physical properties.
3. The modified product of red onion skin extract and cashew nut shell liquid functioned as crude oil emulsion breakers.
4. Increasing demulsifier concentration (from 10 ppm to 50 ppm) and water content of the emulsion increases water separation.
5. Performance evaluation of the formulated demulsifier showed that the effective emulsion breakers in the binary mixture of butanol/ xylene (70:30) performed best.
6. The chemical structure of the formulated emulsion breaker and solvent type, may have increased the partitioning between emulsion phases which enhanced demulsification performance.
7. Optimal water separation of 100% was achieved by MRCNSL product in the binary mixture of Butanol and Xylene in the ratio 70:30 which is because of the attributive synergetic effect of the hydroxyl group.
8. Novel chemical compound of a blend of two extracts MRCNSL has been developed for use as a chemical demulsifier in treatment of crude oil.

6. RECOMMENDATIONS

The economic cost of this reaction should be evaluated. Also the reaction time should be taken into account. The products should also be evaluated for other processes.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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