Original Research Article

Preparation and Evaluation of 1,2-dibromoethane product as oil field emulsion breaker.

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 seperation varied among the solvents. In conclusion, the evaluated MRCNSL products possess 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, synthesis, modification and characterization.

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. (Li et al., 2018). 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. (Orazbekuly et al., 2014).

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. (Venkatesham et al., 2018). 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.

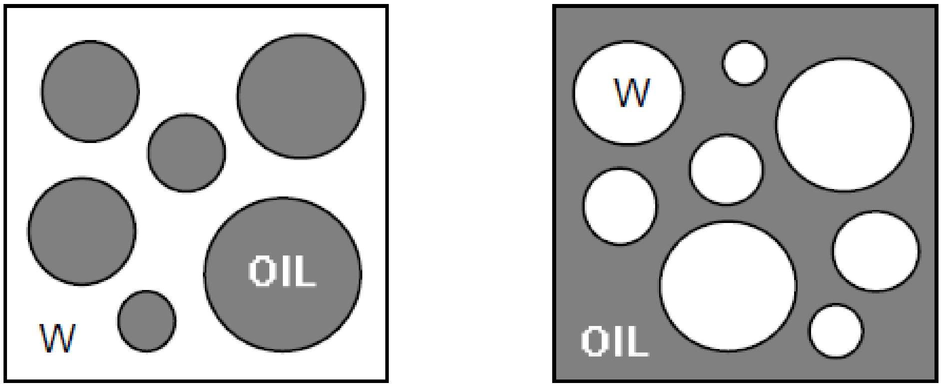
What is an Emulsion?

A nanocrystalline dispersion of two immiscible liquids, such as oil and water, in which one of the liquids is disseminated in the other, is called an emulsion (Mc Clements, 2005). Emulsions can be straightforward or complex. Simple emulsion systems can be divided into two categories, namely:

a. 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.

b. Water-in-oil (W/O) emulsions: In W/O emulsion, water is the dispersed phase which is dispersed in an oil continuous phase (Pradhan *et al.*, 2012).

The diagrammatic representation of simple emulsion is shown in fig 1.1.



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

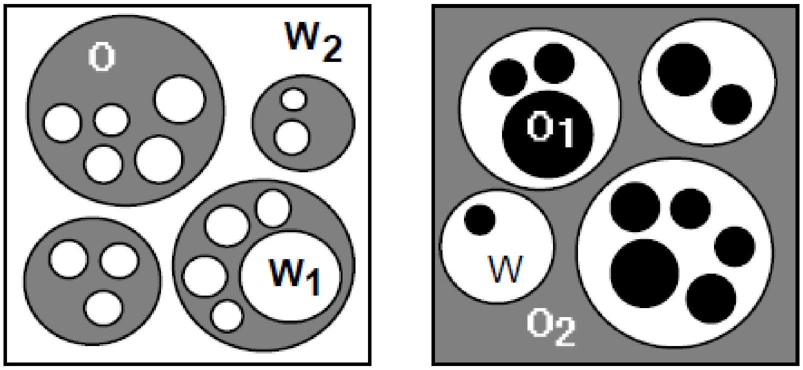
b.Water-in-oil emulsion (W/O)

Fig 1.1 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. (Pradhan *et al.*, 2012).
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 1.2.



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

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

Fig 1.2 Diagrammatic representation of multiple emulsions

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 (Benichou et al., 2001). The inherent stability of the emulsion created is a crucial aspect in determining how effective this procedure is.

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. 1.3. (Raven et al., 1999).

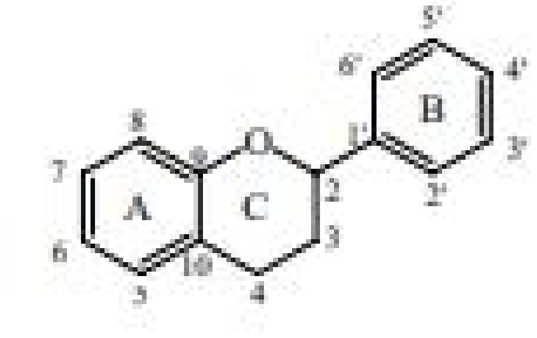


Fig 1.3 Flavan Unit

A significant class of naturally occurring polyphenols known as flavonoids is present in a wide range of plant-based foods (Nilanjan et al., 2015; Chobot et al., 2013). A significant source of carbon produced from plants in the environment is flavonoid compounds. Tannins get into the soil through plant degradation and precipitation. (Liu and Guo, 2015) 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. (Chobot et al., 2013).

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.

For the purpose of this research, flavonoid derivatives (red onion skin extract, it’s derivative and Cashew nut shell liquid derivatives) will be used as a green demulsifier.

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 Lilliaceae 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) (Griffiths et al., 2002). 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 (Sellappan and Akoh, 2002).

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 (Griffiths et al., 2002). It has a high concentration of dietary flavonoids (Slimestad et al., 2007). Compared to the fleshy bulb, these chemicals are more concentrated in the onion skin (Kim and Kim, 2006; Yao et al., 2004; Sellappan and Akoh, 2002).

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.

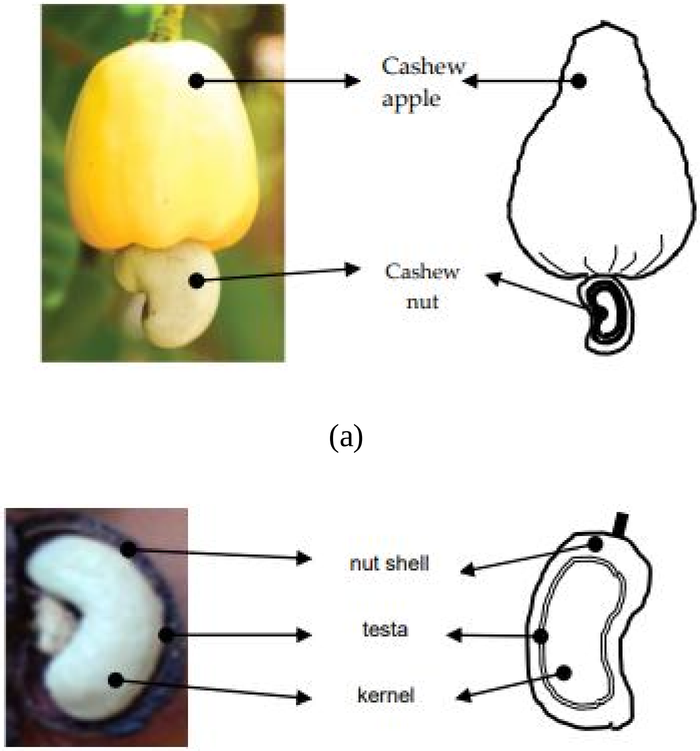
Over the past ten years, major efforts have been made to characterize red onions and the flavonoids found in their skin (Soltoft et al., 2009; Kiassos et al., 2009), which has greatly improved our understanding of these substances. The systematic isolation and identification of flavonoids from red onion skin is still poorly understood despite these investigations. In fig 1.4, the onion bulb and its cross section are shown.

Fig 1.4: Red onion bulb and its cross section.

Cashew Nut Shell

In Nigeria, cashew is widely farmed, primarily for its kernel. The shell is typically seen as waste (Olife et al., 2013). 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 (Gandhi et al., 2012). It is incredibly rich in phenolic lipids such 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 (Mohammed, 2015). 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 (Idah et al., 2014).



.

(a)

(b)

Fig 1.5 (a) Cashew fruit (b) Cashew nut and its cross section

Materials and Method

Materials

Apparatus, Glass Wares and Equipments

They include the following: 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.

Sample Collection and Preparation

Red Onion Skin

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

Cashew Nul Shell Liquid (CNSL)

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 additional investigation.

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.

Methodology

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.

CNSL Extraction

Three hundred grams (300g) 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 70^0C until the solvent becomes clear in the thimble. The extract was named CNSL. The CNSL was recovered from the solvent by distillation technique**.**

Preparation of Flavanoid Derivative

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

Modification of ROSE and CNSL with 1,2-dibromoethane

Quercetin (approx. 8.7 g, 0.029 mol) and powdered potassium carbonate (approx. 0.5g, 0.004mol) were dissolved in cashew nut shell liquid (10mL). The solution was heated to reflux for 15 minutes, then cooled before adding 1,2 dibromoethane (1.2ml). 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.

Sample Characterization

Rose Extract

a. **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.

Specific density $=\frac{mass\ of\ extract}{volume\ of\ extract}$

- Iodine value: 0.50g of the extract was dissolved in carbon tetrachloride in a 100ml conical flask to determine the iodine value. 5mL wijs iodine was added to the flask and left to stand for 2 hours at 25^0C in the dark. The mixture was titrated with 0.1M sodium thiosulphate ($Na_2S_2O_3$) using starch indicator and 5ml potassium iodide (KI) solution. The iodine value was determined using the formula below after performing a blank determination.

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

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 cm^3 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).

$$Free\ fatty\ acid = \frac{28.2 \times V \times N}{W}$$

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 cm^3ethalonic KOH, which was then attached to a condenser for 30 minutes to ensure the sample was completely dissolved. After cooling the sample, 1 cm^3 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.

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

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 cm^3 chloroform and 10cm3 acetic acid in a 22 cm^3 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 $Na_2S_2O_3$ until the yellow color was practically gone. 0.5 cm^3 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.

$Peroxidevalue = \frac{(S-B)\times M\times 1000}{W}$

Where: S= volume of titrant (cm^3) for sample, B= volume of titrant (cm^3) for blank, M= molarity of $Na_2S_2O_3$ solution (in Eq/ cm^3), 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.

$AcidValue$ = Free fatty acid × 1.99

- Refractive Index: This was determined at 20^0C using an Abbe Refractometer (Reichert AR 700). The measurements were performed in triplicate and results were averaged.

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:

Water cut % = $\frac{volume\ of\ water\ collected\ in\ the\ trap}{volume\ of\ sample} \times 100$

- **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:

Kinematic viscosity (cSt) = calliberation constant (c) × Efflux time (in secs)

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

API gravity = $\frac{141.5}{specific\ gravity} - 131.5$

- **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 (3ºC).

- **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.

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.

Specific gravity = $\frac{density\ of\ liquid}{density\ of\ water}$

- **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.

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

- **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.

Resistivity = $\frac{1}{conductivity}$

- **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 ($AgNO_3$)

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

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

Salinity = $Cl^- \times 1.8066$

- pH

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

Sample Preparation

Demulsifier preparation

Five percent weight per weight (5%w/w) of the demulsifier was dissolved in 100 g 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.

Crude oil emulsion preparation

Laboratory simulated emulsions was generated using the approach reported by (Attah et al., 2013 and Atta et al., 2018) 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.

Crude oil emulsion breaking

The bottle testing method, as described by Atta et al., 2013 and Al-Sabagh et al., 2013 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'sperformance was measured in terms of water separation rate, interfacial layer quality, and water separated. The following equation was used to calculate water separation:

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

Results and discussions

Table 1: Characterization of sea water Sample

Parameter	Method	Sea water sample
Total dissolved solids (ppm)	ASTM D 5907	32653
Resistivity (ohm) at 19^0C	ASTM D 1125	0.0181
Conductivity (**µ**S/cm) at 19^0C	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 26^0C	ASTM D 3875	8.18

Table 2: physic-chemical properties of crude oil sample

Parameter	Method	Value
Specific gravity ($60/60^0$F)	ASTM D 1298	0.9030
API gravity at 60^0F	ASTM D 1298	25.1999
Kinematic viscosity at 40^0C (c.St.)	ASTM D 455	13.7506
Kinematic viscosity at 100^0C (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 (^{0}C)	ASTM D 5853	-30

Table 3: 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 (g12/100g)	98.13
Acid value (mg KOH/g)	5.13
Peroxide value meq H_2O_2	2.75
Refractive index	1.46
Free fatty acid	6.93

Table 4: Comparism of Physico-chemical Properties of Extracted CNSL With Literature

Property		literature value	
	Research Value	Idah et al. (2014)	Eke et al. (2019)
Colour	Dark brown	Dark brown	Dark brown
pH	4.06	6.28	5.0
Specific gravity (22.5^{0}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 5 Solubility Test of ROSE, CNSL and their Modified derivative at 25^{0}C

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

Table 1 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 plumping 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 55.41×10^{6} µS/cm furtherconfirms the property of sea water. Likewise the high value of dissolved solids still shows the characteristics of sea water.

Table 2 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 (Al-Sabagh et al., 2013; Atta et al., 2013;2016;2018). They have been classified as medium heavy (according to API classification of oils between 22.3^{0} API and 31.1^{0} 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^{0}C and 100^{0}C respectively which suggests that the crude oil is very viscous, and low pour point value of -50^{0}C suggests low paraffin content.

Table 3 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 4 contains the result of the physic-chemical properties of Cashew nut shell liquid as well as comparism to literature. The result showed that the sample is a brown liquid with pH of 4.06 which indicates acidity. The specific gravity is less than 1while 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 5 shows the solubility test. The result confirms that the solubility of the modified product is not different from the extracts.

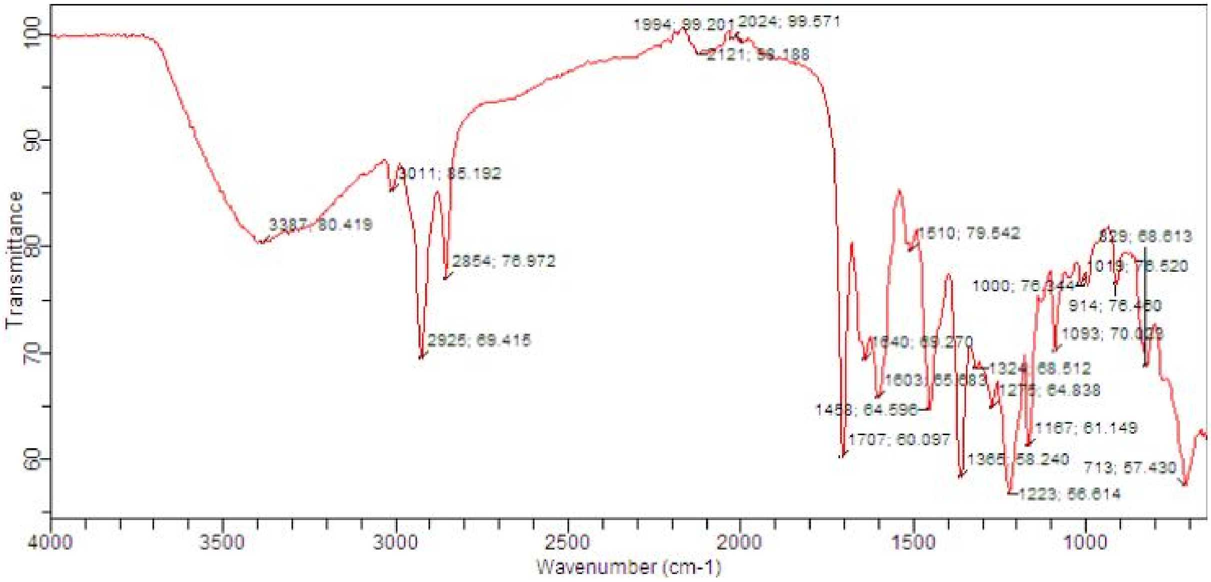


Fig 2 : FTIR Spectrum of MRCNSL

The FTIR spectra of MRCNSL contain typical peaks corresponding to the functional group in quercetin and carnadol, as shown in appendix 4. 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.

Table 6: Demulsification performanceof 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**

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 6. Some factors which influence emulsion breaking were studied and are discussed as follows:

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 6 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, interfacial tension of the emulsion decreases, thus increasing percentage of water separation (Al-Sabagh, 2013).

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 6**, 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, Al-Sabagh et al., 2013, Al-Sabagh et al., 2007).

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, Atta et al., 2013). 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.

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 6. 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 comparism 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.

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 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.

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.

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.

REFERENCES

Al-Sabagh A. M., Nasser N. M., El-Sukkary M. M. A., Eissa A. M. F.& Abd El-Hamid T.M. (2013). Demulsification efficiency of some new stearate esters of ethoxylated and propoxylated 1, 8-Diamino-Octane for water in crude oil emulsions. *Journal of Dispersion Science and Technology*. 34(10):1409-1420.

Atta A. M., Abdullah M. M., Al-Lohedan H. A. & Ezzat A. O. (2013). Demulsification of heavy crude oil using new nonionic cardanol surfactants. *Journal of Molecular Liquids*. 252:311-320.

Atta, A. M., Abdullah, M. M., Al-Lohedan, H. A., & Gaffer, A. K. (2018). Synthesis and application of Amphiphilic poly(ionic liquid) Dendron from cashew nut Shell oil as a green oilfield chemical for heavy petroleum crude oil emulsion. *Energy & Fuels*. 32, 4873–4884**.**

Benichou, A., Aserin, A. &Garti, N. (2001). Polyols, high pressure, and refractive indices equalization for improved stability of W/O emulsions for food applications. *Journal of Dispersion Science and Technology*. 22(2&3): 269-280.

Chobot, V., Kubicova, L., Bachmann, G. &Hadacek, F. (2013). Versatile Redox Chemistry Complicates Antioxidant Capacity Assessment: Flavonoids as Milieu-Dependent Anti- and Pro-Oxidants. *International Journal of Molecular Sciences*. 14, 11830-11841.

Gandhi, T., Patel, M. &Dholakiya B. K. (2012). Studies on effect of various solvents on extraction of Cashew Nut Shell Liquid (CNSL) and isolation of major phenolic constituents from extracted CNSL. *Nat. Prod. Plant Resour.* 2:135-142.

Griffiths, G. T. L., Crowther, T., Thomas, B. & Smith, B. (2002). Onions- A global benefit to health. Phytother. Res., 16 (7): 603-615.

Idah P. A., Simeon M. I., & Mohammed M. A. (2014). Extraction and characterization of cashew nut (*Anacardium occidentale*) oil and cashew shell liquid oil. *Academic Research International*. 5(3):50.

Kiassos, E., Mylonaki, S., Makris, D. P. & Kefalas P. (2009). Implementation of response surface methodology to optimise extraction of onion (*Allium cepa*) solid waste phenolics. *Innov Food Sci Emerg Technol.* 10: 246-52.

Kim, S. J. & Kim G. H. (2006). Quantification of quercetin in different parts of onion and its DPPH radical scavenging and antibacterial activity. *Food Sci Biotechnol*. 15: 39-43.

Li, Z., Geng, H., Wang, X., Jing, B., Liu, Y. & Tan, Y. (2018). Noval tannic acid-based polyether as an effective demulsifier for water-in-aging crude oil emulsions. *Chem. Eng. J.* 354: 1110–1119.

Liu, Y. & Guo, M. (2015). Studies on Transition Metal-Quercetin Complexes Using Electrospray Ionization Tandem Mass Spectrometry. Molecules. 20: 8583-8594.

McClements DJ. (2005). Food Emulsions: Principles, Practices and Techniques. Boca Raton, FL:CRC Press.

Mohammed A. N. (2015). Development of highperformance Cashew Nut Shell Liquid (CNSL) based surface coatings cross linked with styrene and methyl methacrylate (Doctoral dissertation). 6.

Nilanjan, G., Tania, C., Sougata, M., Supriya, M., Deepanwita, S., Balaram, G. &Souvik R. (2015). Synthesis, Characterization and study of antioxidant activity of quercetin-Magnesium complex. *Spectrochimica Acta PartA: Molecular and Biomolecular Spectroscopy*, 151: 807-813

Olife, I. C., Jolaoso, M, A. &Onwualu, A. P. (2013). Cashew processing for economic development in Nigeria. *Agricultural Journal*. 8(1):45-50.

Orazbekuly, Y., Boiko, G. I., Lubchenko, N. P. &Dergunov, S. A. (2014). Novel high-molecular multifunctional reagent for the improvement of crude oil properties. *Fuel Process. Technol*. 128: 349–353.

Pradhan, M., & Rousseau, D. (2012). A one-step process for oil-in-water-in-oil double emulsion formation using a single surfactant. *Journal of Colloid and Interface Science* 386: 398–404.

Raven, P. H., Evert, R. F. & Eichhorn, S. E., (1999). Biology of Plants. 6th ed.; W.H. Freeman: Worth Publishers: New York.

Sellappan, S. &Akoh C. C. (2002). Flavonoids and antioxidant capacity of Georgia-grown Vidalia onions. *J Agric Food Chem.* 50:5338-5342.

Slimestad, R., Fossen, T. &Vagen I. M. (2007). Onions: A source of unique dietary flavonoids. *J Agric Food Chem.* 55: 10067-80.

Soltoft, M., Christensen, J. H., Nielsen, J. &Knuthsen P. (2009). Pressurised liquid extraction of flavonoids in onions. *Method development and validation. Talanta*. 80: 269-78.

Venkatesham, V., Nasal, M., Robin, M. J. &Ginto, G. M. (2018). Studies on Demulsification of Crude Oil Emulsion Using Plant Extracts as Green Demulsifiers. *Asian Journal of Applied Science and Technology (AJAST) (Open Access Quarterly International Journal)*. 2(2):999-1004.