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Francis Moyo and Roman Tandlich*

Optimisation of the emulsion liquid membrane composition and demulsification for rhodium extraction

Abstract: This study was aimed at designing an optimised emulsion liquid membrane (ELM) for the extraction of rhodium from precious metal refinery wastewaters. The demulsification process and the structure of the optimised ELM are reported on. Two optimised ELMs were prepared. The first one contained a 30 % solution of toluene in kerosene as diluent with the following concentrations of the ELM components: 30.000 g/L (w/v) polyisobutylene, 10.870 g/L (m/v) of trioctyl amine and 51.001 g/L (m/v) of SPAN 80. The second ELM contained the same diluent, but the concentrations of the other ELM components in it were as follows: 20.000 g/l of polyisobutylene, 10.268 g/l trioctyl amine and 50.024 g/l of SPAN 80. The stripping phase was the same in both optimised ELMs, namely a 2 M solution of HNO_3. The stripping phase and the diluent solution were mixed together in ratios of 1:1 and 2:1, respectively. Two methods were used to characterise the microdroplet diameters, i.e. optical microscopy and the Zeta-sizer. For the *t*-test, the *p*-value of 0.3018 at 5 % level of significance showed that there was statistically no significant difference in the mean micro-droplet size for 1:2 ELMs containing 20 g/l and 30 g/l of polyisobutylene after 40 minutes of emulsification. The best demulsification results were obtained using the chemical demulsification with polyethylene glycol with molecular weight of 400 g/mol (PEG 400) at 50 ± 1 °C for 24 hours. However, significant carryover of toluene, trioctyl amine and polyethylene glycol into the aqueous phase was observed.

Keywords: Emulsion liquid membrane, polyethylene glycol 400, trioctyl amine, demulsification, polyisobutylene

***Corresponding author: Roman Tandlich:** Division of Pharmaceutical Chemistry, Faculty of Pharmacy, Rhodes University, P. O. Box 94, Grahamstown, 6140, South Africa, E-mail: roman.tandlich@gmail.com

Francis Moyo: Division of Pharmaceutical Chemistry, Faculty of Pharmacy, Rhodes University, P. O. Box 94, Grahamstown, 6140, South Africa

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1 Introduction

Emulsion liquid membranes (ELMs) are semi-permeable systems that have been used in extarction of various classes of chemicals for several decades. New research impetus has been focused on these systems due to the emergence of novel environmental pollutants and the need to recover precious metals from wastewaters due to heightened demand for them. Emulsion droplet size (EDS) of the ELMs is important from the rheology and stability points of view [5]. ELMs of good stability and those that provide rapid extraction have micro-droplet sizes in the range of 0.3-10 μm, with the optimum range from 0.8 to 3.0 μm [10,11]. New extraction devices such as the Taylor-vortex column have recently been applied to the ELM extraction process [15]. The equal distribution of energy increases the stability of the ELMs and should thus improve the recovery of the extracted compounds [15]. Before any extraction experiments can be performed a reproducible ELM preparation method must be available and the recovery procedure optimised. Critical steps in this regard are emulsification and demulsification of the ELMs.

Emulsification is the process of dispersing one liquid in a another one if the two liquids are immiscible [1]. It is a two-stage process: (a) formation of droplets of one liquid in the other and (b) the stabilization of the freshly-formed interface between the two liquids by an emulsifier to prevent re-coalescence of the formed droplets [2-4]. Due to the thermodynamic instability of the newly formed droplets, their coalescence can take place due to Brownian motion and/or the turbulence associated with emulsification [5]. Droplet coalescence can be prevented by the addition of a surfactant [6] or by increasing the viscosity of the ELM [4,7]. Emulsification

can be performed by colloid mills and sonication [8]. It is difficult to produce an ELM of uniform droplet sizes using these methods, i.e. ELMs are mostly poly-dispersed [9]. The ELM extraction efficiency and metal recovery are largely dependent on the ELM demulsification [12], where the loaded ELM microdroplets undergo coagulation or agglomeration [13,14]. Demulsification can be achieved physically or chemically; and its efficiency depends on the ELM surfactant concentration, microdroplet size and the diluent viscosity [12]. Here emulsification and demulsification are optimised for the ELM extraction of rhodium from the platinum-group-metal-bearing wastewaters.

2 Methods

2.1 Apparatus and chemicals

Kerosene, polyisobutylene (PIB) and trioctyl amine (TOA) were purchased from Sigma Aldrich (Johannesburg, South Africa). HNO_3 was purchased from SAARCHEM PTY LTD (Krugersdorp, South Africa), while SPAN 80 and toluene were procured from Fluka Analytical (Johannesburg, South Africa). An Olympus UCMAD3 microscope mounted with an Olympus ultra 20 soft imaging system UTVX-2 was used for all optical microscopy measurements (Institute for Water Research, Rhodes University, South Africa). Absorbances for chemical oxygen demand (COD) were measured using a UV spectrophotometer model UV-1201 (Shimadzu, Johannesburg, South Africa). The Labcon COD thermoreactor model D60 was used for COD digestions (Merck Pty. Ltd., Johannesburg, South Africa) unless stated otherwise. All glassware was purchased from Sigma-Aldrich (Johannesburg, South Africa) and all weights were measured using the PA1214 analytical balance (Pioneer™, Ohaus Corporation, Johannesburg, South Africa). Sonication was done using the BRANSON 8510 ultrasonication bath (LASEC SA, Port Elizabeth, South Africa). Orbital shaking was done using the Chiltern orbital shaker SS70 (Slough, Berkshire, Chiltern Scientific, United Kingdom).

2.2 The ratio of stripping phase to the diluent

For the ELM preparation, 5 g PIB was weighed and transferred quantitatively into a 250 ml volumetric flask and completely dissolved in 150 ml of kerosene. Seventy five millilitres of toluene and 2.5670 g of TOA were added. Both PIB and TOA were completely dissolved in the diluent and the contents of the flask were homogenised by hand-shaking. Then 12.506 g of SPAN 80 was added and dissolved in the solution. Kerosene was used to make up the volume to the mark and the following concentrations were obtained: 20.000 g/l of PIB, 10.268 g/l TOA and 50.024 g/l of SPAN 80. The diluent was mixed with 2 M HNO_3 in the ratios 1:1, 1:2, 1:3 and 1:4; and the mixtures were shaken using the Chiltern SS70 orbital shaker at 600 rpm for 20 minutes. The microdroplet diameters were measured using optical microscopy at a magnification of 400x, or using the Zetasizer. Mixtures were left to stand at 21 ± 2 °C and the time of phase separation was noted. The ELMs were reconstituted and refrigerated at 5 ± 2 °C for 24 hours. The ELMs were re-shaken and the micro-droplet size re-examined to investigate the reusability on different days.

For the other batch of ELMs, 3.000 g of PIB was dissolved in a mixture of 50 ml kerosene and 30 ml toluene, 1.087 g of TOA and 5.1001 g of SPAN 80 were added. All components of the ELMs were completely dissolved by hand-shaking and kerosene was used to make up the volume to the mark. In this way, the following concentrations were obtained: 30.000g/l PIB, 10,870 g/l TOA and 51.001 g/l SPAN 80. The diluent was mixed with 2 M HNO_3 in the ratios 1:1 (10 ml of the nitric acid: 10 ml of diluent) and 1:2 (10 ml of nitric acid: 20 ml of the diluents). The mixtures were then shaken as described in the previous paragraph for 40 minutes and the microdroplet diameter was again measured as mentioned above. The ELMs were left to stand at 21 ± 2 °C and monitored for phase separation. The time taken for significant phase separation to occur was noted. The ELMs were re-made and put in the fridge at 5 ± 2 °C to examine the effect of temperature and the time for phase separation to occur was again noted.

2.3 Micro-droplet size analysis

The average micro-droplet size of the emulsion was measured using photon correlation spectroscopy (PCS) using the Nano-ZS Zetasizer (Malvern Instruments Ltd, Worcestershire, United Kingdom). Before the PCS was done, 30 µl of each sample was diluted using 10 ml of double distilled water in order to obtain a suitable scattering intensity. Ten PCS measurements were performed on each sample at an angle of 90° at 25 °C. The measuring range of the Zetasizer is from approximately 6 nm to 6 µm [18]. Since the presence of particles not in the nano range in dispersion has to be eliminated, it is recommended that PCS be used in combination with laser diffraction (LD), allowing visualization of these particles. LD determines particle size based on detection of diffracted light from the radius of the particles' surface [18,19] In the current

study, it was used in conjunction with optical microscopy. The Olympus UCMAD3 microscope mounted with an Olympus ultra 20 soft imaging system UTVX-2 makes it possible to measure bigger droplet sizes manually. The ELMs were then examined under the microscope above at the magnification of 400x. Approximately Fifteen (15) micro-droplets were examined for each emulsion in ratios of 1:1, 1:2, 1:3 and 1:4. The size of each micro-droplet was manually measured using the optical microscope, the average size, the mode and standard deviation were calculated and results are shown below.

2.4 The effect of time on emulsification and micro-droplet size

The diluent was prepared as described in section 2.2. The diluent was mixed with 2M nitric acid in the ratios 1:1 (10ml of the nitric acid: 10 ml of diluent) and 1:2 (10 ml of nitric acid: 20 ml of the diluents). These were shaken for 20 minutes using an orbital shaker at 600 rpm. Micro-droplet size was measured as described in section 2.3. The ELMs were then examined under the microscope at the magnification of 400x. The ELMs were left to stand at 21 ± 2 °C and monitored for phase separation. The time when significant phase separation occurred was noted. The ELMs were re-made as above and put in the fridge at 5 ˚C to examine the effect of temperature and the time for phase separation to occur was noted. A new set of ELMs was prepared as above. They were then shaken for 40 minutes using an orbital shaker at 600 rpm. Micro-droplet size was measured as described in section 2.3. The ELMs were then examined under the microscope at the magnification of 400x. The ELMs were re-made and put in the fridge at 5 ˚C to examine the effect of temperature and the time for phase separation to occur was noted.

2.5 Thermal demulsification at 35.0 ± 0.5°C

The diluent containing 20 g/l of PIB was prepared like the ones in 2.2 and the diluent containing 30 g/l PIB was prepared in the same way as the one in 2.2 The ELMs were prepared as follows: The diluent with 30 g/l of PIB was mixed with 2 M nitric acid in the ratios 1:2 (20 ml of the nitric acid: 40 ml of diluent) to form two 1:2 ELMs in separate 250 ml Erlenmeyer flasks. One flask was shaken for 20 minutes and the other for 40 minutes using an orbital shaker at 600 rpm. The diluent with 20 g/l of PIB was mixed with 2 M nitric acid in the ratios 1:2 as above. Two 1:2 ELMs were formed and treated as above. All four ELMs were put in the incubator at 35 ˚C for 24 hrs. Unless stated otherwise, all incubations were performed in one of the following incubators: a Labcon incubator Model FSIM B (Labmark, Johannesburg, RSA), a TS 606/3-I incubator (WTW, Weilheim, Germany), a Labcon low temperature incubator LTIE 10 (Labmark, Johannesburg, RSA); and/or a Heraeus Model FT 420 (HeraeusKulzer GmbH, Dormagen, Germany).

2.5.1 Thermal demulsification at 45.0 ± 0.5 °C

The above experiment was repeated with 4 new ELMs - two had the PIB concentration of 20.000 g/l (m/v) and two contained 30.000 g/l (m/v) of PIB. These were placed in the UFE 700 oven (Memmert, Schwabach, Germany) at 45.0 ± 0.5 °C for 24 hours for de-emulsification. The diluent containing 20 g/l of PIB was prepared like the ones in 2.2 and the diluent containing 30 g/l PIB was prepared like the one in 2.5 and the ELMs were prepared as follows: A diluent with 20 g/l of PIB was mixed with 2 M nitric acid in the ratios 1:2 (20 ml of the nitric acid: 40 ml of diluent) to form 1:2 ELMs in 150 ml Erlenmeyer flasks. The flask was shaken for 40 minutes using an orbital shaker at 600 rpm. Five more ELMs were prepared in the same way. Polyethylene glycol with a molecular weight of 400 g/mol(PEG) was added, as shown in Table 1, to the 6 ELMs:

Table 1. The amount of PEG added to each emulsion.

Emulsion	PEG added [g]
1	0
2	1
3	2
4	4
5	6
6	10

The ELMs containing 30.000 g/l of PIB were prepared in an analogical fashion and the same amounts of PEG were added (see Table 1). This resulted in 12 ELMs which were subsequently statically and chemically demulsified using a UFE 700 oven, with the demulsification temperature set to 70 ± 1.0 °C and the incubation period equal to 24 hours. The bottom layer was pipetted and COD was carried out to determine how much of the diluent is in the aqueous phase.

2.5.2 ELM carry-over

After chemical de-emulsification, organic (diluent) layer from the given ELM was removed using a 10 ml glass pipette. Then the bottom/stripping layer from each ELM

was transferred into a clean COD tube and was centrifuged at 3 000 rpm using an Allegra X-15 bench top centrifuge (Beckman Coulter, Johannesburg, South Africa). Once the centrifugation was finished, the COD concentration was measured in the stripping phase (bottom layer). The aim of the measurement was to determine carry-over of the diluent components, extractant and the SPAN 80 into the stripping phase. Subsamples of the stripping phase were removed and examined for the presence of trace emulsion globules under a microscope with the magnification of 400x. This provides an indication of the completeness of phase separation, i.e. the effectiveness of the demulsification process.

The structures and literature values of aqueous solubilities of the individual ELM components were first examined to identify which of the ELM components were responsible for the COD concentrations measured in the stripping phase. SPAN 80 is otherwise known as sorbitan monooleate and it is only dispersible and practically insoluble in water. At the same time, kerosene contains mostly hydrocarbons with limited or negligible aqueous solubility. This was proven by extraction of the stripping phase and measurement of kerosene levels below the LOD of the gas chromatographic method. Given the structure of TOA and the highly acidic pH of the aqueous phase, it is possible for TOA molecules to partition into the stripping phase by formation of ion pairs with nitrate anions from HNO_3 molecules. Molecules of toluene have been shown to undergo hydrogen bonding with molecules of water and its aqueous solubility has been shown to be around 526 mg/l [20]. These two compounds are therefore most likely to contribute significantly to any carry-over of ELM components into the stripping phase during de-emulsification.

The following experiment was performed to measure the actual contribution of TOA and toluene to the COD in the stripping phase after de-emulsification. A fresh batch of the ELM mentioned above was prepared and demulsified in the same fashion. Next, the aqueous phase was placed in a 250 ml separating funnel and 20 ml of n-hexane was added. The contents of the funnel were vigorously hand-shaken for 5 minutes to achieve extraction of organic components. The funnel was left to stand until phase separation was observed and the n-hexane layer was collected into a 100ml volumetric flask. This was then stoppered and extraction was repeated twice with fresh 20 ml aliquots of n-hexane. The three n-hexane extracts were combined and dried with 2.00 g of anhydrous $MgSO_4$(Sigma-Aldrich, Johannesburg, South Africa). Then 20 ml of the organic extract was pipetted into a clean 250 ml Erlenmeyer flaskand three drops of 0.5 % crystal violet (Sigma-Aldrich, Johannesburg, South Africa).The solution was titrated for the TOA content using 0.1 M perchloric acid (solution in acetic acid)as a until the blue colour of the solution changed to a green/yellow colour. All titrations were performed in triplicate and the respective calculations were done according to Eq. (1).

The remainder of the organic extract was concentrated under a gentle stream of nitrogen to 1 ml and transferred into a 2 ml GC vial. The content of toluene was determined using GC analysis. Peak areas were obtained by a splitless injection of 1.0 µL of each of the calibration solutions using a 7693 auto sampler attached to a 7890 gas chromatograph (Agilent, Johannesburg, South Africa) equipped with a DB 5 capillary GC column (30 m × 0.32 µm × 0.25 mm; Agilent, Johannesburg, South Africa) and a flame-ionisation detector. Helium was used as the mobile phase at a flow rate of 1.0 ml/min. The injector and detector temperatures were set to 300°C, and the oven temperature programme was as follows: initial temperature 40°C hold for 3 min, ramp to 180°C at 2.5 °C/min, ramp to 250°C at 20°C/min and hold for 3 min. All gases were purchased in instrument grade from Afrox-Linde(Port Elizabeth, South Africa).

2.5.3 Chemical oxygen demand (COD)

For COD analysis, 3 ml of the aqueous samples were pipetted into the COD test tubes. Then 0.3 ml of reagent A (catalogue number: 1.14679.0495) purchased from Merck (Pty.) Ltd. (Johannesburg/Cape Town, South Africa)and 2.3 ml of reagent B (catalogue number: 1.14679.0495) purchased from Merck (Pty.) Ltd. (Johannesburg/Cape Town, South Africa)were added to each test-tube. The COD test tubes were tightly closed with a screw cap and the contents were mixed using a vortex machine. The samples were incubated at 148 ˚C in a TR-300 thermoreactor for 2 hours. After 2 hours the samples were allowed to cool at 21 ± 2 °C for 15 minutes. Absorbance readings were taken at 600 nm.

2.5.4 Combination of chemical demulsification and thermal demulsification at 50.0 ± 1 °C

The diluents from above in 2.2 were used in this experiment. The diluent with 20 g/l of PIB was mixed with 2M nitric acid in the ratios 1:2 (20 ml of the nitric acid: 40 ml of diluent) to form 1:2 ELMs in 150 ml Erlenmeyer flasks. The flask was shaken for 40 minutes using an orbital shaker at 600 rpm. Ten grams (10 g) of PEG was added and the emulsion was shaken at 600 rpm on the

orbital shaker for 40 minutes. Emulsion containing 30 g/l of PIB was made and treated with PEG in the same way. The two ELMs were placed in an oven at 50 ± 1 ˚C for 24 hrs. The bottom layer was pipetted and chemical oxygen demand (COD) was carried out to determine how much of the diluent is in the aqueous phase.

3 Results

3.1 Emulsification and micro-droplet globule size optimisation

3.1.1 The ratio of stripping phase to the diluent and micro-droplet size

The aqueous phase and the diluent (organic) phase mixed completely to form milky white ELMs. After the first round of shaking, all ELMs remained stable for 3 hours before phase separation took place. Re-emulsification occurred after the shaking was repeated. The 1:1 and 1:2 ELMs subsequently remained stable for 7 hours before phase separation reoccurred. The 1:3 and the 1:4 ELMs remained stable for 12 hours, after which separation occurred. No ELMs were stable beyond 24 hours when stored at 5 ± 2ºC. The average micro-droplet size distribution of 1:1, 1:2, 1:3 and 1:4, as determined using optical microscopy and the Zetasizer, the Zeta potential (ZP), poly-dispersity index (PI) are shown in Table 2 below. Emulsification was done for 20 minutes.

3.1.2 The effect of time on emulsification and micro-droplet size

After 20 minutes, the micro-droplet size distribution indicated that the average diameters, as determined using optical microscopy, of the 1:1 ELMs were 5.8 ± 1.5 µm after storage at 22 ± 1 ºC after 12 hours. The Zetasizer values are shown in Table 3 below. This value was 5.8 ± 2.9 µm after re-shaking and storage at 5 ± 2 ºC for up to 24 hours The average diameters of the micro-droplets with the 1:2 ELMs were 3.4 ± 1.0 µm and 3.3 ± 0.8 µm. The first value is reported for the ELM storage at 22 ± 1 ºC after 12 hours, while the second describes the micro-droplet size distribution after re-constitution of the ELMs through the second shaking for 20 minutes and storage at 5 ± 2 ºC for up to 24 hours.

After 40 minutes, the 1:1 and 1:2 ELMs were stable. There was no phase separation after 12 hours in 21 ± 2 ºC. The average globule diameters, as determined using optical microscopy, of the 1:1 ELMs were 3.1 ± 0.8 µm and 3.5 ± 1 µm. The average diameters of the globules of the 1:2 ELMs are 3.3 ± 0.5 µm and 2.9 ± 0.9 µm. The Zetasizer values are shown in Table 3 below. In both cases, the first average value is reported for ELM storage at 22 ± 1 ºC after 12 hours, while the second describes the micro-droplet size distribution after re-constitution of the ELMs through the second shaking for 40 minutes and storage at 5 ± 2 ºC for up to 24 hours.

The ZP, PI and micro-droplet sizes as determined using the Zetasizer of the 1:1 and 1:2 ELMs containing 20 g/l PIB after shaking for 20 minutes and 40 minutes are shown in Table 3 below.

Table 2: The ZP, PI and micro-droplet sizes as determined using the Zetasizer and optical microscopy of the ELMs after 20 minutes of shaking.

Emulsion	Average micro-droplet size [µm] optical microscope	Average micro-droplet size [µm] Zetasizer	ZP [mV]	PI
1:1	10.8 ± 2.8	5.93 ± 2.8	+ 45	0.65
1:2	4.0 ± 1.6;	4.66 ± 1.9	+ 35	0.57
1:3	11.4 ± 4.6	5.31 ± 3.7	+ 55	0.70
1:4	14.6 ± 6.7	5.69 ± 2.9	+ 67	0.53

Table 3: The ZP, PI and micro-droplet sizes as determined using the Zetasizer of the 1:1 and 1:2 ELMs after 20 minutes and 40 minutes of shaking.

Time of shaking	20 minutes		40 minutes	
Emulsion	**1:1**	**1:2**	**1:1**	**1:2**
ZP [mV]	+ 55	+ 43	+ 47	+ 45
PI	0.54	0.53	0.43	0.47
Average micro-droplet size [µm]	5.31 ± 2.6	4.93 ± 1.0	3.83 ± 0.8	2.34 ± 1.1

3.1.3 Emulsification with diluent containing 30 g/l PIB

For the 1:1 ELMs, average micro-droplet diameters as determined using optical microscopy ranged from 3.0 ± 0.6 µm, 3.2 ± 0.5 µm and 4.1 ± 0.7 µm. The respective values for the 1:2 ELM stood at 3.0 ± 0.5 µm; 2.8 ± 0.4 µm and 2.9 ± 1.0 µm. The Zetasizer values are shown in Table 4 belowFor both types of ELMs, the first average diameter represents the microdroplet size distribution right after the 12 hour storage at 21 ± 2 °C. The second diameter indicates the microdroplet size distribution after the 12 hour storage at 21 ± 2 °C and reconstitution of the ELMs. The last diameter described the changes of the microdroplet diameter distribution after storage of the reconstituted ELM at 5 ± 2°C for 24 hours. Diluent containing 30.000 g/l (w/v) PIB, 10.870 g/l (m/v) of TOA and 51.001 g/l (m/v) of SPAN 80 when mixed with 2 M HNO3 in volumetric ratios of 1:1 or 1:2 leads to the formation of stable ELMs which can be used for up to 12 hours without requiring reconstitution. Storage in the refrigerator is possible after reconstitution and reuse is feasible on two different days.

Table 4: The ZP, PI and micro-droplet sizes as determined using the Zetasizer of the 1:1 and 1:2 ELMs after 40 minutes of shaking.

Time of shaking	40 minutes	
Emulsion	1:1	1:2
ZP [mV]	+ 35	+ 40
PI	0.65	0.55
Average micro droplet size [µm]	3.36 ± 0.6	2.84 ± 1.0

The ZP, PI and micro-droplet sizes as determined using the Zetasizer of the 1:1 and 1:2 ELMs containing 30 g/l PIB after shaking for 20 minutes and 40 minutes are shown in Table 4 below.

3.2 De-emulsification

3.2.1 Chemical, thermal demulsificationand chemical oxygen demand

ELMs after thermal demulsification at 35 ± 0.5°C and 45 ± 0.5°C showed limited or no phase separation after 24 hours. In the combination of chemical demulsification and thermal demulsification, twelve milky white W/O ELMs were formed after 40 minutes of shaking. After the addition of the required amount of PEG and shaking for 75 minutes, the ELMs remained milky white. Phase separation was achieved after the PEG 400 addition and heating of the ELM at 70± 1 °C for 24 hours. There was significant carry-over of ELM diluent components into the stripping phase, as demonstrated by the stripping phase COD concentrations shown in Figure 1. At the same time, no emulsion droplets were detected microscopically in either the stripping phase or the diluent layer.

3.2.2 Combination of chemical and thermal demulsification at 50.0 ± 1 °C

When the chemical demulsification was performed by shaking at 600 rpm for 75 minutes and incubations at 50 ± 1°C, the ELMs lost stability and complete phase separation

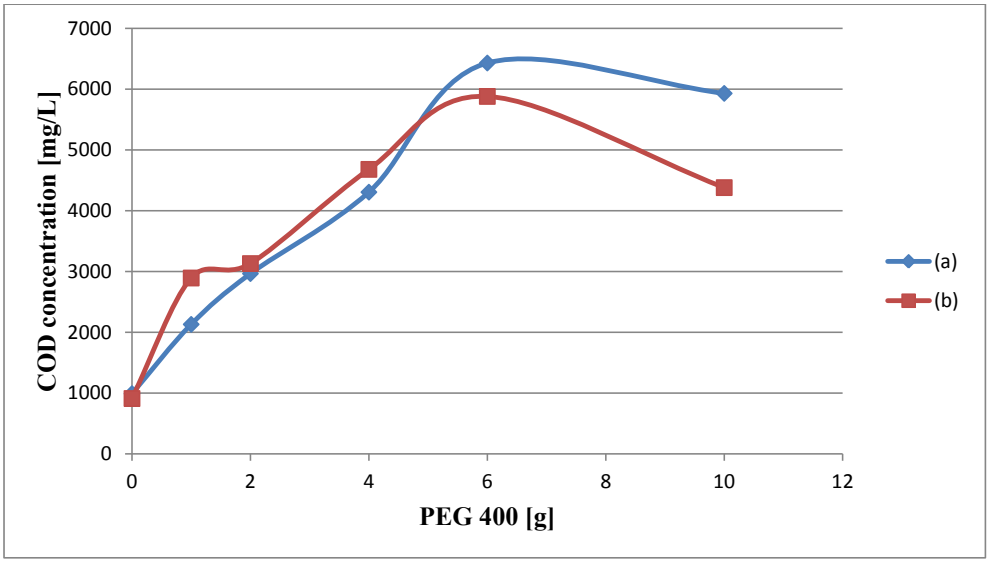

Figure 1: The COD values obtained from the aqueous phase of the demulsified ELMs in relation to the amount of PEG 400 added as a chemical de-emulsifier: (a)COD graph of the aqueous phase of the ELMs containing 20g/l PIB and (b) COD values of the aqueous phase of the ELMs containing 30g/l PIB.

was observed. No ELM micro-droplets were observed in the stripping phase or the diluent.

3.2.3 ELM carryover

Average TOA concentration in the stripping phase was equal to 0.172 g/l. The contribution of these TOA levels to the measured COD concentrations can be estimated using the stoichiometry of the TOA molecule during the COD digestion as shown in Eq. (2):

$$(C_8H_{17})_3N + 36O_2 \rightarrow NH_3 + 24CO_2 + 24H_2O \quad (2)$$

The average volume of stripping phase after demulsification was equal to 15 ml. Combining Eq. (2) with the molecular weights of TOA (353.68 g/mol) and O_2(32 g/mol), the relationship between the TOA concentration and the COD contribution from TOA can be derived to obtain Eq. (3).

$$COD = 3.257 \times C(TOA) = 560 \text{ mg/l} \quad (3)$$

The concentration of TOA is unlikely to be influenced by the weights of the PEG added to the ELM prior to demulsification as this compound is miscible with water and TOA is highly hydrophobic. The average toluene concentration in the stripping phase was equal to 450 mg/l, but the concentrations varied by up to 30 %. Toluene contribution to the measured COD concentrations can be estimated using the stoichiometric Eq. (4):

$$C_7H_8 + 9O_2 \rightarrow 7CO_2 + 4\ H_2O \quad (4)$$

The average volume of stripping phase after demulsification was equal to 15 ml. Combining Eq. (4) with the molecular weights of toluene (92.14 g/mol) and O_2(32g/mol), the relationship between the stripping phase concentration of toluene and the respective COD levels takes the form of Eq. (5).

$$COD = 3.126 \times C(toluene) = 1\,410 \text{ mg/l} \quad (5)$$

4 Discussion

4.1 Emulsification and micro-droplet globule size optimisation

4.1.1 Droplet size

Smaller droplets have higher extraction efficiency as well as better breaking resistance compared to larger droplets [10]. It is imperative that the emulsification process produces smaller micro-droplets. Li et al. [10] also suggested that if the droplets are too small, the emulsion cannot be broken down easily by mechanical methods. This becomes a disadvantage to the ELM process because the ELM must easily break in the demulsification process in order to recover the extracted compound. Therefore the micro-droplet size for the ELM extraction process must be small enough to facilitate efficient extraction but big enough not to create a very stable ELM which cannot be easily demulsified. On the other hand, very large droplets cause the membranes to rupture easily, due to easy coalescence, resulting in poor stability and poor extraction efficiency [21]. Mechanical agitation was used for emulsification because it generates a strong flow field [22]. An orbital shaker at a speed of 600 rpm for 40 minutes was used in the current study. Other studies have shown that speeds up to 24 000 rpm for varying time intervals have been used [23]. Differences in emulsion composition are pivotal in obtaining small micro-droplet diameters at particular speed intervals [22]

Differences in the emulsion composition [11], are important in obtaining ELMs of small micro-droplets size diameter at particular speeds. The average micro-droplet size using the optical microscope in the current study [see Section 3.1.2 b] after shaking at a speed of 600 rpm for 40 minutes were 3.1 ± 0.9 μm and 3.4± 0.9 μm for 1:1 ELMs and 3.3 ± 0.5 μm and 2.9 ± 1.0 μm for the 1:2 ELMs for emulsions which contained 20 g/l PIB. The Zetasizer produced micro-droplet sizes of 3.83 ± 0.8 μm and 2.34 ± 1.1 μm for 1:1 and 1:2 ELMs respectively after 40 minutes, as shown in Table 3. The *t*-test was used to test for the difference between means obtained using the optical microscope and the Zetasizer. The *p* value 0.5465 at 5 % level of significance showed that the difference between the means for the 1:1 ELM was statistically insignificant, while the *p* value: 0.0009, at 5 % level of significance showed that the the difference between the means for the 1:2 ELM was were significant. For highly viscous ELMs formed with 30 g/l PIB, the average micro-droplet size of the 1:1 ELMs were 3.0 ± 0.6 μm, 3.2 ± 0.5 μm and 4.1 ± 0.7 μm and the average diameters of the globules of the 1:2 ELMs are 3.0 ± 0.5 μm; 2.9 ± 0.4 μm and 2.9 ± 1.0 μm using the optical microscope. The Zetasizer produced micro-droplet sizes of 3.36 ± 0.6 μm and 2.84 ± 1.0 μm for 1:1 and 1:2 ELMs respectively after 40 minutes, as shown in Table 4. The *p* values 0.105 and 0.4287 for ELMs containing 30 g/l PIBat 5 % level of significance for 1:1 ELM showed that the difference between the means for the 1:1 ELM was statistically insignificant when using the optical microscope and the Zetasizer. The *p* value: 0.6343 and 0.6619 at 5 % level of significance for 1:2 ELM showed that the difference between the means for the 1:2 ELM was were statistically insignificant when using the optical microscope and the Zetasizer. The *p* values of 0.3018 at 5 % level of significance

for the difference between mean micro-droplet size for 1:2 ELMs containing 20 g/l and 30 g/l PIB obtained using a Zetasizer after 40 minutes shows that there was statistically no significant difference in micro-droplet size for 1:2 ELMs containing 20 g/l and 30 g/l PIB.

4.1.2 Emulsification speed and time.

In the current study, two time intervals of 20 minutes and 40 minutes were used. For 1:1 emulsion, the average droplet diameter was 5.8± 1.5 μm and 5.8 ± 2.9 μm and, for 1:2 emulsions, the average droplet sizes were 3.4 ± 1.0 μm and 3.4 ± 0.8 μmusing the optical microscope. Most droplets were so small that it was difficult to measure them as they were below 3 μm, hence the Zetasizer was utilized. As shown in Table 3 after 20 minutes of shaking, the micro-droplet sizes were 5.31 ± 2.6 μm and 4.93 ± 1.0 μm. Zetasizer and optical microscope results were comparable for the 1:1 emulsion. All results were confirmed using the Zetasizer and are shown in Table 3.

These are in agreement with other studies. It has been reported that emulsification speed and time have a direct effect on the droplet size. Droplet size decreases as the emulsification speed and time increase [24-26]. In studies on the effect of speed and time of emulsification reported by Venkatesan et al. [24,49], w/o ELMs were prepared using a speed of 2 000 – 12 000 rpm at different time intervals of between 2 – 10 minutes, and they obtained an optimum emulsification time of 6 mins at 10 000 rpm. In another study, optimum emulsification time and speed obtained was 5 mins and 7 000 rpm respectively, where w/o ELMs were made using a speed of range of 3 000 rpm – 8 000 rpm from between 2 – 10 minutes [25]. In the current study, a lower speed was used for a longer time, whilst in these cited studies high speeds were used for a shorter time interval. Studies have shown that higher speeds, compared to the 600 rpm used in this study, have been used to produce smaller micro-droplets. A speed of 12 000 rpm for 30 minutes to produce micro-droplets of 3.35, 3.424 and 2.72 μm [27,28] and in another study, micro-droplets of 2.13 and 1 μm at the speed of 7 000 rpm for 20 minutes were produced [29]. These differences are due to differences in emulsion compositions.

4.1.3 Volume ratio of stripping phase to the diluent

The ratio of volumes of stripping phase to diluent has been studied and it has a significant impact on the stability of the emulsion and the extraction process [11,30,31]. In this study, ratios of 1:1, 1:2, 1:3, and 1:4 (stripping phase: diluent) were examined. The ratio of 1:2 produced ELM with small droplet sizes and hence, by implication, it was more stable and had a better extraction ratio, as discussed in Section 4.1.2. The 1:3 and 1:4 produced very large droplets of diameters 11.4 ± 4.6 μm and 14.6 ± 6.7 μm respectively. The Zetasizer was used to verify these results. From Table 2, the average micro-droplet diameter for 1:1, 1:2, 1:3 and 1:4 were 5.93 ± 2.8 μm, 4.66 ± 1.9 μm, 5.31 ± 3.7 μm and 5.69 ± 2.9 μm respectively. These results are not comparable to the ones of the optical microscope. But they are still outside the 0.8 to3 μm range which will make a preferable emulsion [10,11]. It has been reported that increasing the decreases emulsion stability. Increasing the volume of the stripping phase leads to the increase in the droplet diameter which in turn leads to easy coalescence of the droplets, reducing the stability of the membrane. Increasing the volume of the stripping phase also leads to leakage of the stripping solution into the external/feed phase [32,33,33-35]. When the volume of the stripping phase is increased beyond a certain critical point, the membrane phase becomes insufficient to cover the disperse phase [36] hence the micro-droplets of the stripping phase are not wholly covered by the surfactant, leading to an increase in the interfacial tension resulting in coalescence and membrane instability. It has also been reported that the lower the more stable the membrane, the higher its resistance is to breakage, the higher the osmotic swelling and entrainment and the less the diffusion process [37-39]. Less diffusion process, higher osmotic swelling and an increase in entrainment may lead to low extraction efficiency. Hence it is important to select the optimum ratio which is high enough not to impede the diffusion process, high enough not to increase osmotic swelling and entrainment but which is also low enough not to lead to emulsion instability by increasing the droplet sizes and reducing extraction efficiency. For this study, the ratio of 1:2 was used according to the results obtained in Section 3.1.3.

4.1.4 The choice of a diluent

The choice of the diluent is also important for emulsion stability. The diluent should be compatible with the surfactant and the extractant. Its solubility in the internal and external phase should be negligible and its density should be different to that of the aqueous phase. In this study, kerosene was used because it has been widely and successfully used as a diluent in different studies of ELM [30,40-42]. Viscosity of the diluent plays an important part

in stability of the membrane. Non-Newtonian modifiers like PIB have been used to increase the viscosity of the diluents [15,43,44]. PIB was used in the current study to modify the viscosity of the diluent [kerosene and toluene]. Dissolving PIB in a mixture of kerosene and toluene took 24 hours, with shaking at the speed of 100 rpm. Toluene was chosen because it has been successfully used as a diluent in other studies [39,45,46]. Hence 30 % of toluene was used and PIB dissolved in 7 hours of shaking at a speed of 100 rpm. For comparison of the effect of viscosity on emulsion droplet size and extraction, ELMs containing concentrations of 20 g/l and 30 g/l of the PIB were used in this study. Using 30 g/l of PIB, globule size of a 1:1 emulsion after 40 minutes of shaking were 3.0 ± 0.6 μm, 3.2 ± 0.5 μm and 4.1 ± 0.7 μm. The globule sizes of a 1:2 emulsion after 40 minutes were 3.0 ± 0.5 μm; 2.8 ± 0.4 μm and 2.9 ± 1.0 μm. Taking the above-mentioned data leads to the conclusion that there was no significant change in droplet size diameter between ELMs containing 20 g/l and 30 g/l of PIB, as described in Section 4.1.2.

4.1.5 Surfactant concentration

In this study a concentration of 5 % w/v of SPAN 80 was used as the surfactant. This concentration was chosen based on the literature review of the emulsification process of the ELMs with SPAN 80 as a surfactant. In a study by García, Acosta et al. (2013) [40], the concentration of SPAN 80 was varied from 0% to 3 % w/v. It was concluded that emulsion stability increases with increases in SPAN 80 concentrations. Optimum extraction was obtained at 2 % w/v SPAN 80. They also stated that 3 % of SPAN 80 formed super stable ELMs which were difficult to break and that very low surfactant concentrations of 0-0.5 % produced unstable ELMs resulting in approximately 0 % extraction of chromium. In a similar study by Chanukya, Rastogi(2013) [11], concentration range of SPAN 80 used was 2-4 %. It was discovered that extraction increases with increases in SPAN 80 concentrations until the concentration of SPAN reaches an optimum, in which case extraction begins to drop. In a different study by Goyal, Jayakumar et al. (2011) [31], 3 % of SPAN 80 resulted in the maximum extraction of chromium. The concentration range of SPAN 80 used was 1 – 5 %. Above 3 %, the extraction efficiency decreased. Therefore surfactant concentration is vital in the stability and extraction of the membrane. The lower the concentration the more unstable the ELM becomes. When concentration is increased above the critical micelles, aggregate formation takes place in the bulk. Micelles, reverse micelles and surfactant hydration cause breakage and osmotic swelling as they promote the transportation of water from the feed phase to the internal phase. As the surfactant concentration increases the mass transfer resistance is enhanced [47-49].

4.1.6 Zeta potential and poly-dispersity index

The zeta potential can be used to predict the physical stability of the emulsion [50-52]. For excellent physical stability, a minimum zeta potential of greater than ±60 mV is mandatory and greater than ±30 mV is needed for good physical stability [19,53]. The ZP of the 1:1, 1:2, 1:3 and 1:4 ranged from + 35 mV to + 55 mV (see Table 2) soon after manufacture, meaning that they were relatively stable, and the ZP fell in the range of ±60 mV. Only the 1:4 ELMs had a ZP of +67 mV, which is outside the range and it can be concluded that it was the least stable emulsion. There was no significant difference in the ZP in the study of effect of time on emulsification and micro-droplet size (Section 3.1.2). The ZP in the 1:1 emulsion was + 55 and + 47 mV for 20 and 40 minutes respectively and + 47 mV and + 43 mV for 1:2 emulsion for 20 and 40 minutes respectively (Table 3). From Table 4, the ZP for ELMs prepared using 30 g/l PIB were within the range of stability. Zeta potential decreases with an increase in the energy (light and temperature) of the system due to increased particle kinetic energy thus particle aggregation and gelation [54]. So to maintain the stability of the emulsion, it was important to keep them in a temperature controlled environment, for example in the fridge. PI is defined as the measurement of the width of the distribution of these particle sizes. In this case, PI is going to be the measurement of micro-droplet sizes. The PI ranges from 0 to 1. In a mono-disperse system, the PI should be 0. PI increases for very broadly distributed particles [18]. The PI from Table 2 ranges from 0.53 to 0.70. This is an indication that the micro-droplets are not mono dispersed. This means the micro-droplets are of varying sizes. 1:3 ELMs had the largest PI, meaning that, for this emulsion, the difference between the smallest micro-droplets and the largest micro-droplets was large. In Table 3, the PI ranged from 0.43 to 0.54. The ELMs shaken for 40 minutes had a lower PI of 0.3 and 0.47 for 1:1 and 1:2 ELMs respectively. From this it can be concluded that the effect of time on emulsification affects the PI of micro-droplet size. The longer the emulsification time, the better the PI.

4.2 Demulsification, ELM carryover and COD

Heat was first used for demulsification. Two temperatures were used: 35 ˚C and 45 ˚C. After 24 hours, demulsification was not achieved. Demulsification efficiency using heat only for ELMs stabilized by SPAN 80 surfactant is very low [55]. Hence there was a need to add a chemical de-emulsifier. The heat was increased to 70˚C and a chemical de-emulsifier, PEG 400, was introduced. Al-Sabagh et al (2013) [13] stated that sometimes a combination of the chemical and the physical approach are necessary for successful demulsification to take place. Hence, in this study, a combination of the chemical approach (PEG 400) and the physical approach (heat) was used. For successful chemical de-emulsification, selection of the chemical de-emulsifier is vital. The quantity and duration of mixing of the de-emulsifier with the emulsion, and the sufficient time to allow the de-emulsifier to coalesce and settle the droplets are also factors to be considered [13]. The quantity of the PEG which was optimum for successful demulsification was examined using PEG quantities varying from 1g -10g. After 24 hours of heating, the ELMs containing the chemical de-emulsifier were successfully demulsified. The diluent which floated on the aqueous phase was orange in colour, which was not the original colour of the diluent. This could have been due to the chemical change of the chemicals composing the diluent resulting from high temperatures and the addition of PEG. The aqueous phase had an orange colour, indicating that, although demulsification was achieved, some of the diluent was still in the aqueous phase. This led to the examination of the amount of carbon content in the aqueous phase using COD. COD is used to indirectly measure the amount of organic compounds in water. This follows the logic that organic compounds are oxidised fully to form carbon dioxide in the presence of a strong oxidising agent under acidic conditions [56] .

Another important discovery was that the higher the HLB value for the chemical de-emulsifier the better a de-emulsifier it becomes. The w/o ELMs are formed using surfactants with low HLB values and the o/w ELMs are formed using surfactants with high HLB values. Hence, chemicals with high HLB values are likely to demulsify water in oil ELMs. The HLB of PEG is 11.6, which is higher than that of the SPAN 80 [HLB 4.3][57] used as a surfactant in the ELMs. Al-Sabagh et al (2013)[13] stated that chemical de-emulsifiers usually have a high molecular weight and a higher HLB value than the surfactant used to stabilize the emulsion so as to be able to destabilize the emulsion. PEG reduces the stability of the interfacial film, leading to the coalescence of the aqueous phase, hence demulsification. It has been stated that in chemical demulsification, the stability of the interfacial film is reduced by increasing the film-thinning rate by addition of a chemical demulsifier. This chemical demulsifier destabilizes the surfactant-stabilized emulsion films by altering the interfacial rheological properties. The interfacial activity of the demulsifier must be high enough to suppress the interfacial tension gradient, thus accelerating the rate of film drainage and promoting coalescence [58]

The duration of mixing the chemical de-emulsifier with the emulsion is also important to successful demulsification. PEG was mixed with the emulsion for 75 minutes. All these ELMs were heated at 70˚C for 24 hours and all were demulsified. The temperature was then reduced to 50˚C since it was suspected that 70˚C was chemically altering the diluent. At 50 ˚C the ELM containing 6 g of PEG, had not yet demulsified completely, hence 10 g at 50 ˚C was done. At 50 ˚C, demulsification was achieved fully when the amount of added PEG was 10 g. This is because the concentration of the demulsifier must be sufficient enough in the droplets to ensure a high enough diffusion flux to the interface [14,59]. It was noted that, as the concentration of the PEG increased in the emulsion, COD values also increased, as shown in Figure 1. This is due to the fact that PEG is an o/w surfactant since it has the ability to partition in water as much as it is oil soluble. Hence some PEG is in the water, increasing the COD. Kim et al [14] stated that for the chemical de-emulsifier to be good, it has to partition into the aqueous phase [14]. Other authors in another study of demulsification of Petroleum ELMs using oil-soluble de-emulsifiers reached the same conclusions [59].

It has to be stated, however, that the carry-over of organic matter is variable. These data were taken into account during the study as the loss of diluent components increases the cost of any developed ELM extraction method. Prices for the extractant, diluent and the chemical demulsifier vary significantly and, therefore, it is critical to ascertain which one of these components is likely to contribute to the COD concentrations shown in Figure 1. The concentration TOA is unlikely to be influenced by the weights of PEG added to the ELM prior to demulsification, as this compound has been shown to be miscible with water and will not influence TOA mass transfer into the aqueous phase. Summation of the TOA and toluene contributions to the COD levels in the stripping phase account for 1 970 mg/l. The remaining COD concentrations most likely originate from oxidation of the PEG molecule, which dissolves in water during chemical demulsification. This also explains the increase of COD with the increase of PEG observed in Figure 1.

5 Conclusions

The emulsification process was successfully developed and optimum conditions of emulsification for this study were: a) The stripping phase: diluent ratio was 1:2; b) the mechanical agitation speed was 600 rpm and the emulsification time was 40 minutes; c) 5% of the surfactant SPAN 80 was used and d) There was no significant difference in the ELMs containing 20 g/l PIB and 30 g/l PIB in terms of the droplet size. The demulsification technique was successfully optimised. Optimum conditions for demulsification were heating the emulsion for 24 hours at a temperature of 50˚C. The chemical de-emulsifier, PEG, used was 10 g and mixed with the emulsion for 75 minutes before heating.

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