Report

on

Minor Research Project

funded by

Nirma University

Development of Low Cost Method for Breaking Kinetically Stable Emulsions

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Final Report for Nirma University Funded Minor Research Project

1.	**Project Title:**	Development of low cost method for breaking kinetically stable emulsions
2.	**Name of the Principal Investigator:**	Dr. Amita Chaudhary and Dr. Ankur Dwivedi
3.	**Project Approval Letter No. and Date:**	NU/DRI/MinResPrj/IT/2019-20/ dated 03rd February 2020
4.	**Date of the Project Commencement:**	01/04/2020
5.	**Progress Report No.**	2
6.	**Period of Report:**	
	From (dd/mm/yyyy):	01/04/2020
	Up to (dd/mm/yyyy):	30/06/2021
7.	**Details of the Committee Members (Name, Designation)**	
	Member -1	Dr. Sanjay Patel, HoD & Professor, CH, ITNU
	Member -2	Dr. Jayesh Ruparelia, Professor, CH, ITNU
	Member -3	Dr. Milind Joshipura, Professor, CH, ITNU
8.	**Details of Fund Utilization:**	
	Total Budget Sanctioned (in Rs.)	1,00,000/-
	Total Expenditure Incurred (in Rs.)	45644.22/-
9.	**Please enclose a summary of the work done so far and results achieved.**	Attached
10.	**Attach copy of the papers published / presented, etc., if any.**	In preparing stage
11.	**Is the work progress as per the original plan of work and towards achieving the objectives? If not, state reasons.**	No, due to the non-working of hiring services in COVID-19
12.	**Any other Information:**	N/A

Submitted by: Dr. Amita Chaudhary and Dr. Ankur Dwivedi

Endorsed by:

Committee Members:

Dr. Sanjay Patel, HoD & Professor, CH, ITNU

Dr. Jayesh Ruparelia, Professor, CH, ITNU

Dr. Milind Joshipura, Professor, CH, ITNU

Closure Report (April 2020 to June 2021)

1. Objectives of project

- Development and characterization of Oleophilic ionic liquid.
- Preparation of emulsions O/W and check its stability rate.
- De-emulsification experiment using ionic liquid and iron nano particles.
- Parametric studies like concentration of IL, mass of nano particles, temperature, stirring rate, etc.
- Recovery of Ionic liquid and Magnetic nano particles from oil.

2. Introduction

The kinetically stable oil-in-water emulsions are widely used in chemical industries for cooling and lubrication of contacting metal surfaces. Such types of emulsions have high specific heats and heat transfer coefficients, which make them operable under high temperature and pressure conditions. Besides, many merits, they have some environmental issues. Although there is a number of conventional techniques available for the breaking of such emulsions, such as acidification, centrifugation, electrolytic method, UV radiation, and membrane separation, but these all are energy-intensive, and harmful to the environment. Thus, there is a need for a new cost-effective, eco-friendly, and less energy-intensive treatment method. In the present work, we proposed a new method for breaking such kinetically stable emulsion via magnetic nanoparticles (MNPs) for physical separation and chemical dissolution method using oleophilic ionic liquid.

Emulsion is produced when two or more immiscible liquids mix vigorously together which results in two phases (a dispersed phase and a continuous phase) [1][2]. The phase that has smaller volume is usually identified as the dispersed phase and the larger one is the continuous phase. If the volume of both phases are the same, other factors would be considered to recognize the dispersed and continuous phases[3][4]. Based on the Bancroft rule, a continuous phase would be the phase that emulsifying agents are more soluble in it [5].

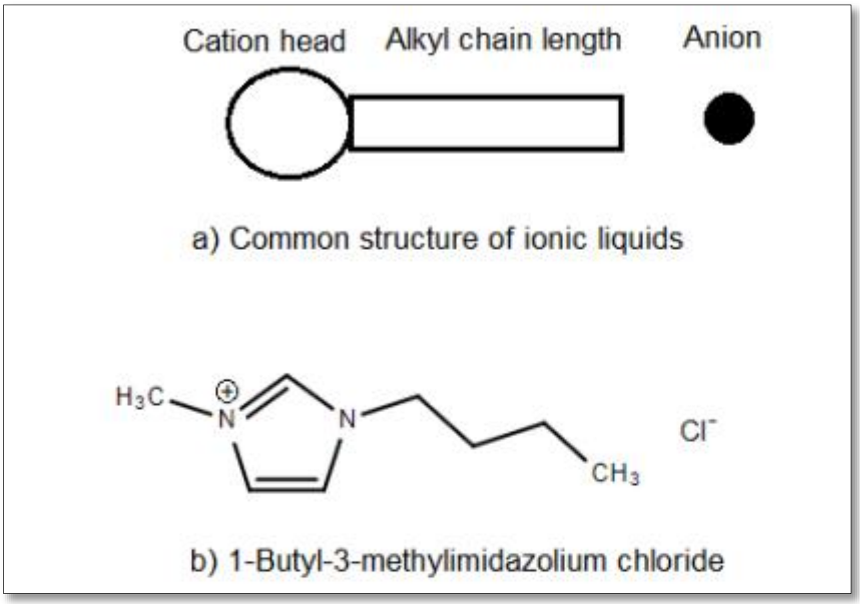
Emulsion Types:

According to the nature of the dispersed phase, emulsions are categorized into oil in water (O/W), water in oil (W/O) and multiple (W/O/W or O/W/O) types. O/W emulsions occur when oil droplets are the dispersed phase (inner phase) in the continuous water phase (outer phase), which is also called reverse emulsion. W/O emulsions are generated when water droplets are the dispersed phase in the continuous oil phase. Multiple emulsion is a mixture of W/O and O/W emulsions. O/W/O emulsions are formed when oil droplets are the dispersed phase in water droplets that are dispersed in the continuous oil phase, while W/O/W emulsions are formed vice versa. It should be noted that these emulsions are thermodynamically unstable but are kinetically stable. Emulsions are thermodynamically unstable because they are produced from the mixture of two or more immiscible liquids which naturally tend to separate. However, the kinetic stability of emulsions means that emulsions are stable for weeks to years due to the formation of strict films around them by emulsifiers [6].

Many research studies have been conducted for the application of ionic liquids in chemical demulsification processes, and it was reported that ionic liquids are reliable demulsifiers with high stability, even under high temperature and high salinity [7]. Ionic liquids are produced by a combination of different organic cations and organic or inorganic anions[8]. They are associated with unique characteristics such as thermal stability, non-flammability, recyclability, and low vapor pressure. These properties make ionic liquids a suitable substitute for organic solvents and commercial demulsifiers [9]. Ionic liquids have been used by different researchers to evaluate their efficiency in demulsification processes, mostly at the laboratory scales.

Proposed mechanism:

The amphiphilic character can be introduced by tailoring the composition of ionic liquid. Figure 5 shows the common structure of ionic liquids used in the research work and the structure of 1-butyl-3-methylimidazolium chloride.



The demulsification mechanism of ionic liquids involves two main steps, including diffusion and adsorption. The diffusion process is the distribution of ionic liquid molecules in the continuous phase before arriving at the O-W interface, while the adsorption process means that the diffused ionic liquid molecules pass through the continuous phase and reach the O-W interface[10]. The ionic liquid molecules then substitute natural emulsifying agents at the interface and change the viscoelastic properties of the interfacial films. This leads to breaking the strong film around O-W droplets and enhancing the coalescence of the dispersed droplets [11]. Recent investigations have found that hydrophobic surface-active ionic liquids can be used for effective demulsification of W/O emulsions in the oil and gas industries [12].

To evaluate the demulsification efficiency of ionic liquids, bottle test is commonly used in laboratories [13]. In a bottle test, an ionic liquid is added dropwise to a graduated settling tube containing emulsions. Then their mixture is shaken for 1–5 min, followed by the measurement of the height of the separated water and oil at different time [14]. The demulsification efficiency is calculated using Equation (1):

$$DE = \frac{C_i - C_f}{C_i} \times 100 \quad \ldots\ldots\ldots(1)$$

Here, DE is demulsification efficiency, Ci is the initial oil (water) concentration of emulsion, and Cf is the final oil (water) concentration of emulsion.

Combination of Ionic Liquids with MNPs:

Recent investigations demonstrated that the presence of nanoparticles with ionic liquids or other demulsifiers in a system could enhance the interfacial properties and the demulsification process. The enhancement may be because demulsifier molecules adsorb on the surface of nanoparticles and create large particles which push them to move towards the O-W interface and break the interfacial film [15]. Another method was reported to coat ionic liquids onto the surface of nanoparticles to achieve promising results [16]. Atta et al. in their research investigated the effect of 1-allyl-3-methylimidazolium oleate (AMO) coated magnetic nanoparticles (Fe3O4) at different concentrations (magnetic to oil ratio 1:10, 1:20, 1:25, 1:50) to remove oil from water, and found that 90% of oil was removed from water at the lowest concentration of magnetic nanoparticles capped with AMO (1:50).

Due to the nano range, the particles have a high surface energy. Because of this high surface energy, the stabilizer of the emulsion (soap solution or surface active agent) dissociates itself from the oil and adsorbs onto the particles. This results in the separation of very fine droplets of oil. As per the literature, iron nano-particles are oleophilic (oil has a very strong affinity for nanoparticles). The oil droplets therefore get adsorbed on the nano particles. Then they will make settled using magnetic effect.

Experimental Work

All the chemicals were purchased from the CDH and Merck of analytical grade. These chemicals are used without any further purification.

Synthesis of Ionic Liquid

The oleophilic ionic liquid was synthesized by the proton transfer method between a acid and a organic base. An equimolar quantity of inorganic acid and organic base were taken for synthesis. Initially, the imidazolium base is charged in a three-necked round bottom flask fitted with a reflux condenser, mechanical stirrer, and a pressure funnel as shown in Fig.3.1. The hydrochloric acid was added drop by drop using the pressure funnel in the base solution with constant stirring. Since this protonation reaction is highly exothermic, the reactor was placed in an ice-bath. The mixture was then stirred at ambient conditions for several hours. To ensure complete reaction, a slight excess (~10-15%) of the organic base was used. The product was washed three times with dichloro methane (DCM) to remove the unreacted reagents. [17]

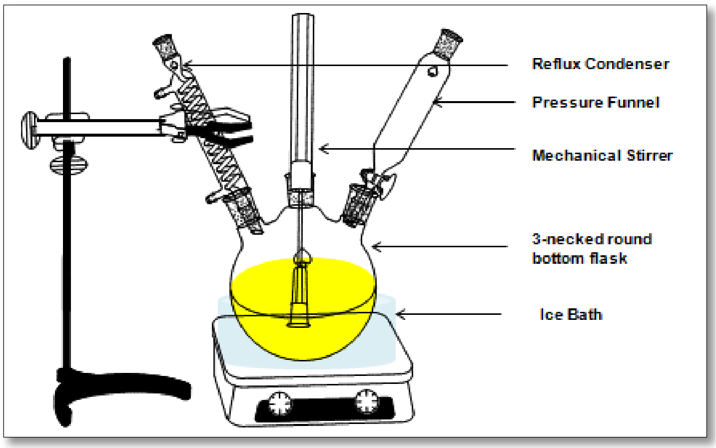


Figure: Experimental Setup for synthesis of ionic liquid (1 butyl-3- methyl imidazolium chloride)

The product was kept at 80 $^{\circ}$C in a vacuum oven further for 24 hours to remove traces of DCM and moisture and the final product is ready to analyze. A similar procedure was followed to synthesize all ionic liquids with the same organic base but, different organic acids.

Synthesis of O/W Emulsion

One mL of castor Oil is added continuously in 100 ml of water with 1.2 g Sodium dodecyl sulfate as anionic surfactant for 4 h at reflux temperature of 40 ^{o}C with continuous stirring.

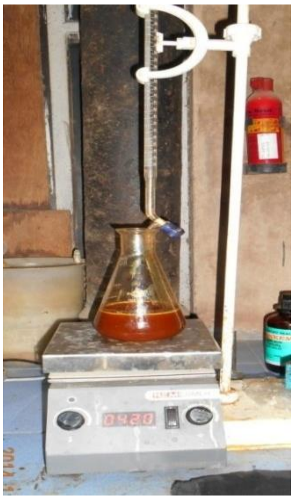


Figure: Experimental setup for emulsion breaking with ionic liquid and nano particles

Emulsion Stability Test

The standard test method (ASTM 263) for emulsion stability was carried out for the synthesized emulsion. Emulsion stability was tested on 5 and 10% solutions of soluble oil in distilled water, which contains 0.688 g/L of $CaSO_4 \cdot 2H_2O$ to give hardness of 400 ppm in terms of $CaCO_3$. In this test, the emulsion was prepared at 5 or 10% soluble oil percentages as follows:

100mL of tap water is taken in a a 250 mL conical flask. Add 5 mL of the formulated emulsion in it with continuous stirring for 2 min. This flask was left for 24 h to check emulsion stability. The emulsion stability can be observed with no oil layer separation after 24 h.

In the de-emulsification experiment

In the demulsification study, 10 g of MNPs are added to 100 mL of O/W emulsion. The solution was stirred for 1 hr. After some time, due to the coning effect, oil is adsorbed over the MNPs and settled down in the bottom of the beaker. Afterward, the flask is placed on a rectangular magnet due to which all the nanoparticles along with oil adhere with the magnet. The water present in the upper layer of the beaker is decanted out and measured.

Magnetic Nano Particles **Emulsion** **Recovered water** **Recovered Oil**

In the turbidity test, the emulsion sowed 400 NTU, whereas the recovered water shows only 5 NTU.

Recovery of Nano particles

During the study of recovery of MNPs from the first batch of 100 ml of emulsion treatment, 0.7g of MNPS. The recovered MNPs from the first batch was used in the treatment of second fresh batch of emulsion (100 mL). In the second attempt, 0.65g recovered. Similarly, when experiment was repeated with third batch of fresh emulsion, it was found that the recovered MNPs were not able to break the emulsion completely. So, to that, fresh 0.5 g MNPs were added to break the emulsion completely. It was observed that MNPs could be reused thrice with a little amount of fresh addition of MNPs.

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