

Investigation of choline based ionic liquids as an oil spill dispersant

Mansoor Ul Hassan Shah¹, Magaret Sivapragasam², Muhammad Moniruzzaman^{1,2,*}, Md. Mahabubur Rahman Talukder³ and Suzana Bt Yusup¹

¹Department of Chemical Engineering, Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Perak, Malaysia

²Centre of Research in Ionic Liquids (CORIL), Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Perak, Malaysia

³Institute of Chemical and Engineering Sciences (ICES), Agency for Science, Technology and Research, 627833, 1 Pesek Road, Jurong Island, Singapore

*m.moniruzzaman@utp.edu.my

Abstract. Chemical dispersants are universally used to overcome oil spill damages. However, the toxicity related with chemical dispersants minimizes its usage as oil spill dispersants. Thus, the employment of biodegradable and environmental benign dispersants in marine environment is much needed. In this research, the capability of choline myristate [Cho][Myr] and choline oleate [Cho][Ol] were investigated to be used as oil spill dispersants. Results reported in this study illustrates that by combining these two amphiphilies, an effective dispersion is achieved. A maximum dispersion of 71 % was achieved by combining [Cho][Myr] and [Cho][Ol] with an optimal ratio of 60:40 (w/w). The dispersant to oil ratio (DOR) was 1:10 (v/v) at this optimal combination. Further, by increasing the DOR the effectiveness increases and about 78% dispersion is achieved at 1:1 (v/v). Moreover, the blend of [Cho][Myr] and [Cho][Ol] at 60:40 (w/w) ratio formed a stable emulsion than its single components.

1. Introduction

Several oil spills occurred in the past, for instance, in the year 2010 Deepwater Horizon (DWH) oil spill occurred due to which about 4.9 million barrels of oil was transferred to the sea [1, 2]. Similarly, about 2000 barrel of oil was shifted to the Gulf of Mexico in the year 2000 [3]. In the same way Exxon Valdez oil spill (in year 1989) released about 11 million gallons of crude oil to the Gulf of Alaska [4]. In Malaysia, there remains a regular risk of oil spill and about 121 cases of oil pollution reported in between the year 2009 and 2015 [5].

When dispersants are applied, it reduces the interfacial tension between oil and water. The wave action transfers the large oil slick to discrete droplets and the adsorbed surfactant molecules stabilizes each droplet [6]. The stabilized oil droplets are dispersed through the water surface, and with the passage of time most of the oil is degraded by ocean microbes [7].

The dispersant toxicity is one of the basic parameter to be considered before the employment of dispersants to the sea environment [8]. Accelerated environmental awareness and strict rules has made dispersants environmental compatibility a key factor in their applications [9, 10]. A blend of surfactants is used in the recent research for overcoming oil spill damages [11, 12]. Although Corexit is the most employed formulation in this regard, the components and solvent used in its formulation are



nonbiodegradable and toxic. [13]. Therefore, various researches have endeavored to determine the oil spill dispersant formulations as a replacement to the conventional toxic dispersants [14, 15].

Choline based ionic liquids has recently attracted plenty of attention of academia and researchers [16]. They are used exclusively in various fields including; biomass pretreatment, carbon dioxide adsorption and as demulsifying agent [16, 17]. In this research, the capability of choline-based biocompatible ionic liquids (ILs) as oil spill dispersants were explored. Two choline based ILs, [Cho][Myr] and [Cho][OI] (figure 1 A) and B)) were synthesized and combined with different proportion using water as a solvent.

2. Experimental

2.1. Materials

The chemicals employed to synthesize the ionic ILs include; myristic acid (Merck, New Jersey, USA), oleic acid (Sigma, St. Louis, Missouri, USA), and choline hydroxide (46 wt% water, Sigma-Aldrich, St. Louis, Missouri, USA). The chemicals were used as supplied without any further purification. Appropriate amount (about 1%) of salts were dissolved in distilled water to prepare synthetic sea water. Crude oil emulsions were prepared by employing Tapis crude oil (provided by the Petroleum Industry of the Malaysia Mutual Aid Group).

2.2. Synthesis of choline based ILs

A previously reported method was employed for the synthesis of [Cho][Myr] and [Cho][OI] [18]. In this method, the required acid was imparted to the aqueous choline hydroxide solution with a molar ratio of 1:1 at 25°C. The mixture was continuously stirred, and the reaction mixture was refluxed for 24 h at 80°C. The synthesized ILs were then dried in rotary evaporator (BUCHI, Switzerland) under vacuum (80°C, 2 h). Figure 1 (A and B) representing the molecular structures of the synthesized ILs.

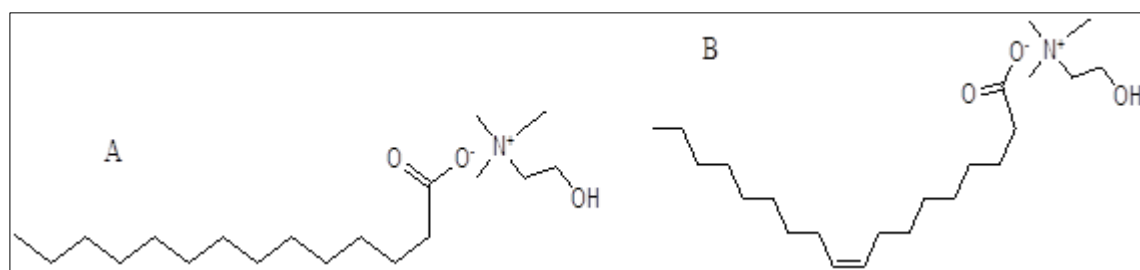


Figure 1. Structure of choline based ILs A) Choline myristate B) Choline oleate.

2.3. Measurement of interfacial tension

The crude oil and synthetic sea water interfacial tension (IFT) was measured using the pendant drop method (OCA20, Data Physics). In this method, the synthetic sea water was placed in a glass tube followed by injection of dispersant crude oil mixture. The IFT was evaluated by drop shape analysis. The IFT of the pure components as well as of the combined system were investigated by mixing appropriate volume of the stock solutions of [Cho][Myr] and [Cho][OI].

2.4. Baffled Flask Test (BFT)

The effectiveness of dispersant was determine using U.S.A Environmental Protection Agency (EPA) revised protocol [19]. In the Baffled Flask Test (BFT), 120 mL of synthetic sea water was introduced in the baffled flask. Then 100 μ L of crude oil was gently dispensed onto the surface of synthetic sea water. On the top of crude oil, 4 μ L dispersant was poured carefully so that the dispersant should not touch the water first. This gives dispersant-to-oil ratio (DOR) of 1:25. Different DOR was obtained by varying

the dispersant volume while keeping the oil volume constant. The solution was then mixed by placing the flask in an orbital shaker (at 200 rpm) for 10 min. Allowing a settling time of 10 min, 30 mL sample from the center of the flask was then taken and the dispersed oil in the aqueous sample was extracted with dichloromethane (DCM). Absorbance readings at 340, 370 and 400 nm was recorded by utilizing a spectrophotometric measurement. The dispersant effectiveness was calculated using equation

$$Eff(\%) = \frac{Total\ Oil\ Dispersed}{\rho_{oil}V_{oil}} \times 100 \quad (1)$$

ρ_{oil} = Density of Tapis crude oil

V_{oil} = Volume of Tapis crude oil added to the test flask

2.5 Emulsions preparation

Crude oil emulsions were prepared by adding 1 mL of crude oil to 10 mL of synthetic sea water. Appropriate amount of dispersant was added, and the sample was then placed on a vortex mixer for 3 min. After emulsion preparation, vials were placed on the benchtop for visual observation at room temperature (25°C). Images were taken over a period of time to evaluate the stability.

3. Result and discussion

3.1. Interfacial tension

The IFT between sea water and crude oil were evaluated and the DOR was kept constant at 1:10 (v/v) for all measurements. The IFT of pure and combined system of [Cho][Myr] and [Cho][OI] are presented in figure 2. It is expected that both [Cho][Myr] and [Cho][OI] pack closely at oil water interface due to favorable interactions between both the tails of [Cho][Myr] and [Cho][OI]. As it can be seen that [Cho][OI] tail has one cis unsaturation and their existence ensures that the tail remain flexible and liquid like at room temperature. Therefore, the flexible, bent tail of [Cho][OI] may aid in the packing of these molecules close to each other and results in low IFT compared to its pure components. This lower IFT of the mixture as compared to its pure components is due to the synergistic interaction between the molecules and this synergistic interaction was maximum at 60/40 (w/w) ratio of [Cho][Myr] and [Cho][OI] which resulted in least IFT (2.18 mN/m). Athas *et al.* [20] noticed a similar trend where the IFT of the mixture (Lecithin and Tween 80) was less than individual components IFT, showing the synergism between the components. IFT results presented in this research work illustrates the synergistic behavior of the two components ([Cho][Myr] and [Cho][OI]).

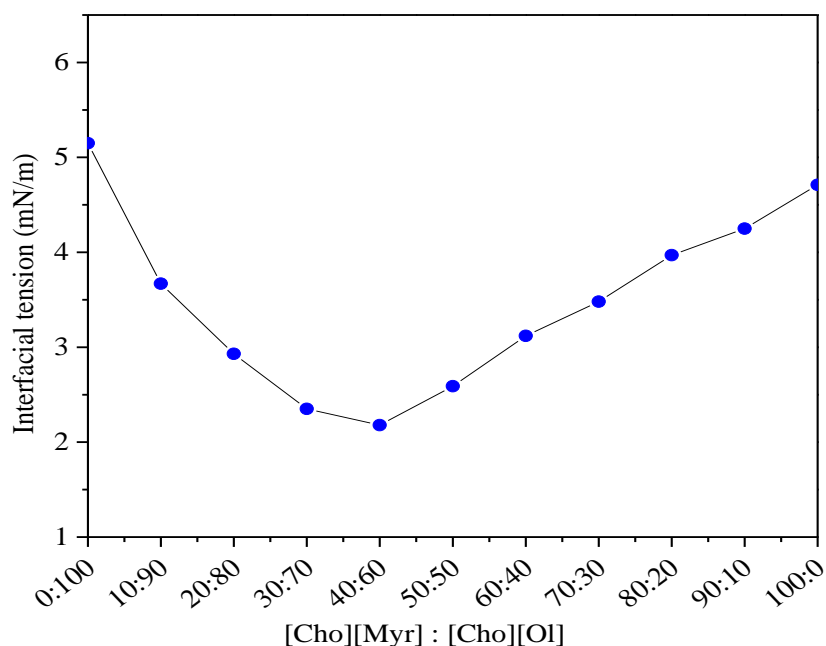


Figure 2. Interfacial tension of [Cho][Myr] and [Cho][Ol] at different ratio (w/w) of two components at 25 °C.

3.2. Effectiveness of dispersant

The dispersants effectiveness was determined using BFT (as mentioned in section 2.4) and the results are presented in figure 3 as a function of [Cho][Myr] and [Cho][Ol] (w/w) ratio. It was noticed that the individual components exhibited less effectiveness as compared to the combined system. The most effective dispersion was achieved at 60:40 ratio of [Cho][Myr]: [Cho][Ol]. At this optimal ratio 71% effectiveness was observed. The IFT measurement (figure 2) between sea water and crude oil (DOR 1:10 (v/v)) revealed that low IFT is achieved at this ratio. The sharp decrease in IFT explains the corresponding high effectiveness at this optimal ratio. Further, for [Cho][Myr]:[Cho][Ol] ratios other than 60:40, results in high IFT, which accounted for the decline in dispersant effectiveness.

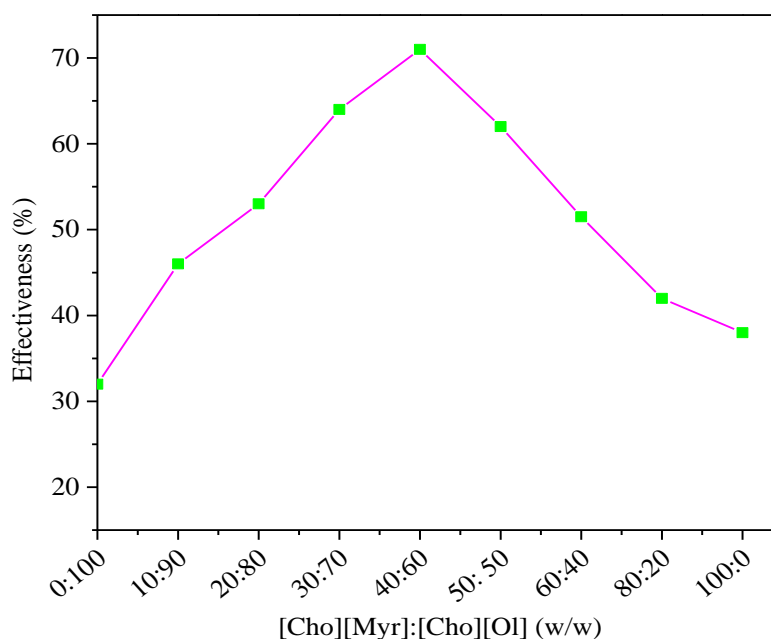


Figure 3. Effectives of dispersant at different [Cho][OI] and [Cho][Myr] ratios. The DOR was kept constant at 1:10 (v/v) for all combinations.

3.3. Dispersant oil ratio

The effectiveness of dispersant over a range of DOR are presented in figure 4. The dispersant consists of 60:40 [Cho][Myr]: [Cho][OI] (w/w), the most effective [Cho][Myr]: [Cho][OI] ratio (figure 3). The DOR used in this work include; 1:1, 1:10, 1:25, 1:50 and 1:100, and it was observed that the effectiveness increased by increasing the DOR. The highest effectiveness of about 78 % was achieved at 1:1 DOR. This high effectiveness at high DOR is due to the fact that small oil droplets formed at high DOR, which are more stable compared to the larger oil droplets, hence resulting in high effectiveness. The results presented in this work are in line with the previous study conducted by Nyankson *et al.* [21], observed high effectiveness at high DOR.

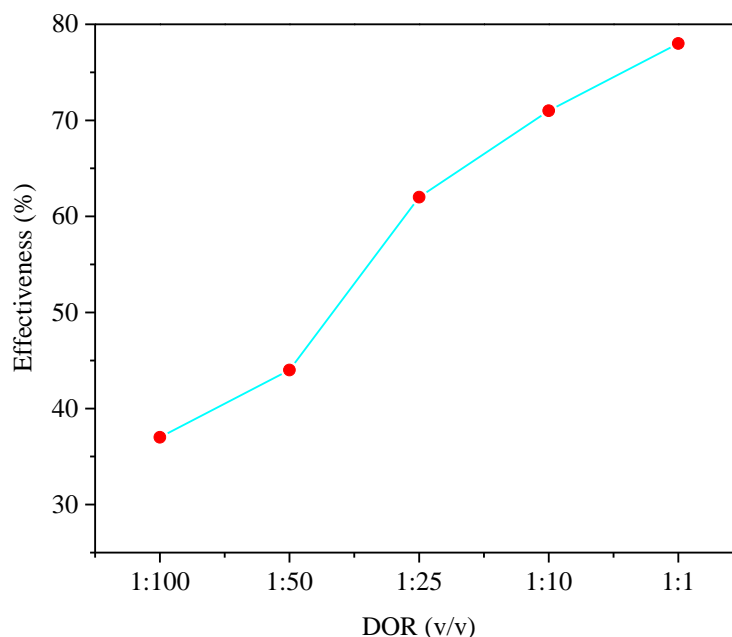


Figure 4. Effectives of dispersant at different DOR. The composition of the components are 60:40 ([Cho][Myr]:[Cho][OI]) for all DOR.

3.4. Crude oil and water emulsions

Crude oil sea water emulsions were prepared by maintaining the oil water ratio at 1:10 (w/w) and presented in figure 5. A dispersant oil ratio of 1:1 (w/w) was kept constant for all experiments. Results presented in figure 5 are for three cases: [Cho][Myr] alone, [Cho][OI] alone and a 60:40 ratio of [Cho][Myr] and [Cho][OI]. For the first two cases initially, a homogeneous brown coloured emulsion is formed (at $t = 0$ min) after vortex mixing. However, after 30 min of vortex mixing the oil droplets rises to the top by forming a distinct layer of oil above the aqueous phase, indicating that the emulsions in both cases are unstable. In contrast, the emulsion prepared with 60:40 ratio of [Cho][Myr] and [Cho][OI] behaved differently. In this case, the emulsion formed at ($t = 0$ min) and after 30 min are almost identical and there is no indication of oil separation from aqueous phase. Therefore, we can infer from visual observations that blend of [Cho][Myr] and [Cho][OI] formed a much stable emulsion and acted as an efficient dispersant than either its stand alone components.

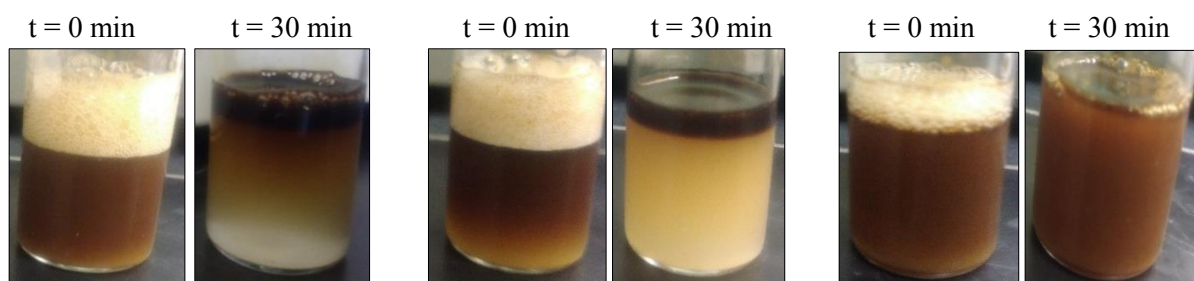


Figure 5. Emulsification formed between crude oil and sea water (a) 100% [Cho][OI] (b) 100% [Cho][Myr] (c) 60% [Cho][Myr] + 40% [Cho][OI].

4. Conclusion

In this study the choline based ILs were employed to combat oil spill issues. The most effective [Cho][Myr] and [Cho][Ol] mixture ratio is 60:40 (w/w). A stable emulsion was observed at this ratio compared to the individual components. At this optimal ratio, the dispersant effectiveness was 71 % having DOR 1:10 (v/v). For ratio [Cho][Myr]:[Cho][Ol] higher/lower than this, effectiveness is decreased by high interfacial tension. Furthermore, by increasing the DOR ratios the effectiveness increases, and 78 % effectiveness is achieved at 1:1 (v/v). Moreover, instead of toxic organic solvents, water was used as a solvent which will ultimately make it an environmentally benign dispersant.

Acknowledgements

The authors would like to gratitude, centre of research in ionic liquids (CORIL), Universiti Teknologi PETRONAS, Malaysia for providing research facilities and funding (0153AA-E35). M.U.H Shah gratefully acknowledge the financial assistance through Graduate Research Assistance (GRA) scheme by the centre of research in ionic liquids (CORIL), Universiti Teknologi PETRONAS.

References

- [1] Kostka J E, Prakash O, Overholt W A, Green S J, Freyer G, Canion A, Delgardio J, Norton N, Hazen T C and Huettel M 2011 Hydrocarbon-degrading bacteria and the bacterial community response in Gulf of Mexico beach sands impacted by the Deepwater Horizon oil spill *App. and env. micro.* **77** 7962-74
- [2] Gong Y, Zhao X, Cai Z, O'reilly S, Hao X and Zhao D 2014 A review of oil, dispersed oil and sediment interactions in the aquatic environment: influence on the fate, transport and remediation of oil spills *Marine pol. bul.* **79** 16-33
- [3] Stoermer S, Butler G and Henry C 2001 *Application of dispersants to mitigate oil spills in the Gulf of Mexico: The Poseidon Pipeline spill case study* International Oil Spill Conference: American Petroleum Institute 1227-9
- [4] Carson R T, Mitchell R C, Hanemann M, Kopp R J, Presser S and Ruud P A 2003 Contingent valuation and lost passive use: damages from the Exxon Valdez oil spill *Env. and res. eco.* **25** 257-86
- [5] Hamid A G 2017 Filling the legal vacuum in combatting maritime crimes: a law reform strategy for Malaysia *Int. J. of Public Law and Policy* **6** 1-20
- [6] Board O S 2005 *Oil spill dispersants: efficacy and effects. Committee on Understanding Oil Spills: Efficacy and Effects* National Research Council National Academies Press, Washington
- [7] Varadaraj R, Robbins M, Bock J, Pace S and MacDonald D 1995 *Dispersion and biodegradation of oil spills on water* International Oil Spill Conference: American Petroleum Institute 101-6
- [8] Almeda R, Hyatt C and Buskey E J 2014 Toxicity of dispersant Corexit 9500A and crude oil to marine microzooplankton *Eco. and env. safety* **106** 76-85
- [9] Maier R and Soberon-Chavez G 2000 Pseudomonas aeruginosa rhamnolipids: biosynthesis and potential applications *App. Micro. and Biotech.* **54** 625-33

- [10] Shah M U H, Sivapragasam M, Moniruzzaman M, Talukder M M R, Yusup S B and Goto M 2017 Production of sophorolipids by *Starmerella bombicola* yeast using new hydrophobic substrates *Bio. Eng. J.* **127** 60-7
- [11] Wang A, Li Y, Yang X, Bao M and Cheng H 2017 The enhanced stability and biodegradation of dispersed crude oil droplets by Xanthan Gum as an additive of chemical dispersant *Marine pol. bul.* **118** 275-80
- [12] Michel J, Adams E, Addassi Y, Copeland T, Greeley M, James B, Mcgee B, Mitchelmore C, Onishi Y and Payne J 2005 *Oil spill dispersants: efficacy and effects* The National Academy of Sciences: Washington, DC
- [13] Nyankson E, DeCuir M J and Gupta R B 2015 Soybean lecithin as a dispersant for crude oil spills *ACS Sus. Chem. & Eng.* **3** 920-31
- [14] Owoseni O, Nyankson E, Zhang Y, Adams S J, He J, McPherson G L, Bose A, Gupta R B and John V T 2014 Release of surfactant cargo from interfacially-active halloysite clay nanotubes for oil spill remediation *Langmuir* **30** 13533-41
- [15] Nyankson E, Olasehinde O, John V T and Gupta R B 2015 Surfactant-loaded halloysite clay nanotube dispersants for crude oil spill remediation *Ind.l & Eng. Che. Res.* **54** 9328-41
- [16] Gadilohar B L and Shankarling G S 2017 Choline based ionic liquids and their applications in organic transformation *J. of Mol. Liq.* **227** 234-61
- [17] Aburto J, Márquez D M, Navarro J C and Martínez-Palou R 2014 Amphiphilic Choline Carboxylates as Demulsifiers of Water-in-Crude Oil Emulsions *Ten. Surfac. Deter.* **51** 313-7
- [18] Petkovic M, Ferguson J L, Gunaratne H N, Ferreira R, Leitao M C, Seddon K R, Rebelo L P N and Pereira C S 2010 Novel biocompatible cholinium-based ionic liquids—toxicity and biodegradability *Green Chem.* **12** 643-9
- [19] Sorial G A, Venosa A D, Koran K M, Holder E and King D W 2004 Oil spill dispersant effectiveness protocol. II: Performance of revised protocol *J. of Env. Eng.* **130** 1085-93
- [20] Athas J C, Jun K, McCafferty C, Owoseni O, John V T and Raghavan S R 2014 An effective dispersant for oil spills based on food-grade amphiphiles *Langmuir* **30** 9285-94
- [21] Nyankson E, Demir M, Gonen M and Gupta R B 2016 Interfacially active hydroxylated soybean lecithin dispersant for crude oil spill remediation *ACS Sus. Chem. & Eng.* **4** 2056-67