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Characterization and Demulsification of Water-in-crude Oil Emulsions

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Abstract: Many advances have been made in the field of emulsions in recent years. Emulsion behavior is largely controlled by the properties of the adsorbed layers that stabilized the oil-water surfaces. The effect of chemical demulsifiers in demulsification of water-in-crude oil emulsions were assessed experimentally. The relative rates of water separation were characterized via graduated beakers. Four groups of demulsifier with different functional groups were used in this work namely amines, polyhydric alcohol, sulphonate and polymer. The effect of alcohol addition on demulsification performance also studied. The results obtained in this study have exposed the capability of chemical demulsifiers in destabilization of water-in-crude oil emulsions. Further works are nevertheless required to provide deeper understanding of the mechanisms involved to facilitate the development of an optimum system applicable to the industry.

Key words: Demulsification, crude oil emulsions, chemicals, alcohol, interfacial tension

INTRODUCTION

Water is normally present in crude oil reservoirs or is injected as steam to stimulate oil production. Water and oil can mix while rising through the well and when passing through valves and pumps to form in most cases relatively stable dispersions of water droplets in crude oil (w/o), which are usually referred to as oil field emulsions. Formation of these emulsions during oil production is a costly problem, both in terms of chemicals used and due to production losses. Therefore, the breaking of emulsions (destabilization) is necessary in many applications such as environmental technology, painting, coating and petroleum industry. Chemical destabilization is the most widely applied method of treating water-in-oil (w/o) emulsions and involves the use of chemical additives to accelerate the emulsion breaking process. For economic and operational reasons, it is necessary to separate the water completely from the crude oil before transporting or refining them. In petroleum system, asphaltene and resinous substances comprise a major portion of the interfacially active components of the oil (Sjoblom *et al.*, 1992; Johansen *et al.*, 1989; Urdahl *et al.*, 1992; Corbett and Petrossi, 1978; Shiffert *et al.*, 1984). Anklam (1997) reported that in the oil industry, water comes into contact with crude oil on many occasions, creating emulsions stabilized by various components in the oil, including the asphaltene and resins. At drilling

sites, the recovered oil will contain some water and hydrophilic impurities which need to be removed before shipping and processing. There are many methods for the neutralization and reduction of the emulsifying agent has been used, for example, Hanessey *et al.* (1995) used the gravity separation, while electrostatic coalescence has used by Bailes *et al.* (1997), chemical demulsification used by Abdurahman *et al.* (2006), centrifugal and filtration methods mentioned by Lissant (1983) as techniques used for breaking the emulsion.

The objective of this research is to study the effect of chemical additives on breaking emulsions. Experimental results showed that, addition of alcohol to chemical demulsifiers will highly accelerate the process of emulsion demulsification.

MATERIALS AND METHODS

To accomplish the objective of this study, the crude oil samples were obtained from Petronas Refinery at Melaka. A detailed procedure for the water-in-oil (w/o) emulsions preparation and their procedures including the formation of w/o emulsion, their characteristics and method of preparation are thoroughly described in a previous research by Abdurahman *et al.* (2006). Here the work merely describes the main experimental steps. Water-in-crude oil emulsions were prepared by dispersing distilled water in crude oil at room temperature with a

standard three blade propeller at speed of 1600 rpm. Relevant properties of the crude oil are listed in Table 1. Triton X-100 used beside asphaltenes and resins originally present in the crude oil to stabilize the emulsions. The emulsifying agent was used as received

Table 1: Crude oil analysis

Property/component	Units	Value
API	-	26.200
Viscosity	cp	18.400
Density	g cm ⁻³	0.852
SARA analysis:	-	-
Saturates	wt %	60.000
Aromatics	wt %	25.800
Resins	wt %	13.500
Asphaltene	wt %	1.500

without any further dilution. The prepared emulsions were used to check for w/o or o/w emulsions. All emulsions investigated were found w/o emulsions type (oil continuous phase).

Four chemical demulsifiers were used to perform demulsification tests. These chemicals were; amine groups, polymeric, sulphonate and polyhydric alcohol demulsifiers. The chemical demulsifiers used were listed in Table 2. While the interfacial pressure of various demulsifiers related to the percentage of water and oil separation is presented in Table 3. The ability of these chemicals to destabilize w/o emulsions were evaluated from the volume of water observed in the beaker as follows:

Table 2: The chemical additives used in emulsion demulsification tests

Groups	Demulsifier	Concentration (mole L ⁻¹)	HLB No.
A: Polymeric	Polyethylene block PEG	800.00	8.30
	Poly PO terminated	800.00	7.32
	Polyethylene Oxide (PEO) 600,000	0.2485	8.80
	Polyethylene Oxide (PEO) 1000,000	0.2485	8.88
B: Polyhydric alcohols	Polyethylene glycol (PEG) 600	0.2485	13.20
	Ethylene glycol (EG)	0.2485	9.85
	Propylene glycol (PG)	0.2485	9.40
	Polyethylene glycol (PEG) 1000	0.2485	16.00
C: Amines	Hexylamine	0.2485	6.98
	Trioctylamine	0.2485	15.00
	Dioctylamine	0.2485	6.75
	Octylamine	0.2485	6.88
	Pentylamine	0.2485	6.87
	Propylamine	0.2485	6.86
	Decylamine	0.2485	6.93
	Sodium di-2-ethylhexyl sulphosuccinate (AOT)	0.0013	13.65
D: Sulphonate	Dodecyl benzene sulphonic acid (DBSA)	0.0013	7.35
	Sodium dodecyl benzene sulphonic (NaDBS)	0.0013	-

Table 3: The interfacial pressure of various demulsifiers related to the percentage of water and oil separation

Demulsifier	IFT (mN m ⁻¹)		Interfacial pressure Ω (mN m ⁻¹)	Percentage of separation (v/v)	
	γ _o	γ _a		Water	Oil
A: Polymeric					
Polyethylene block PEG	30.5	27.7	2.8	2	15
Poly PO terminated	30.5	28.6	1.9	0	8
Polyethylene Oxide (PEO) 600,000	30.5	38.5	-8.0	20	62
Polyethylene Oxide (PEO) 1000,000	30.5	35.8	-5.3	8	46
B: Polyhydric alcohols					
Polyethylene glycol (PEG) 600	30.5	25.5	5.0	40	55
Ethylene glycol (EG)	30.5	27.8	2.7	7	25
Propylene glycol (PG)	30.5	29.4	1.1	0	15
Polyethylene glycol (PEG) 1000	30.5	24.6	5.9	46	58
C: Amines					
Hexylamine	30.5	25.2	5.3	64	74
Trioctylamine	30.5	39.4	-8.9	30	47
Dioctylamine	30.5	29.5	1.0	43	58
Octylamine	30.5	24.5	6.0	67	77
Pentylamine	30.5	27.8	2.7	57	68
Propylamine	30.5	28.5	2.0	25	39
Decylamine	30.5	23.0	7.5	80	87
D: Sulphonate					
Sodium di-2-ethylhexyl sulphosuccinate (AOT)	30.5	26.4	4.1	38	68
Dodecyl benzene sulphonic acid (DBSA)	30.5	30.8	-0.3	18	73
Sodium dodecyl benzene sulphonic (NaDBS)	30.5	28.5	2.0	15	70

$$(\text{Water separated \%}) = \frac{\text{Volume of separated water (mL)}}{\text{Original volume of water in the emulsion (mL)}} \times 100 \quad (1)$$

RESULTS AND DISCUSSION

Demulsification is the breaking of a crude-oil emulsion into oil and water phases. From a process point of view, the oil producer is interested in two aspects of demulsification; the rate or speed at which this separation takes place and the amount of water left in the crude oil after separation. The stability of the emulsions was determined visually by measuring the water and oil separation from emulsions at 30°C as a function of time. In terms of emulsion characterization, this study used a variety of surfactants to get a high stability for water-in-oil emulsions. Coalescence needs to be minimized to obtain any useful rheological information. In this regard, as shear rate increases, the viscosity decreased. Figure 1, the viscosity data shown in Fig. 1 indicate that the emulsions exhibit Newtonian behavior up to a water content of 20% (this is indicated by constant values of viscosity for all shear rates or a slope of zero). At water cuts above 20%, the slopes of the curves deviate from zero, indicating Non-Newtonian behavior. Also, the Non-Newtonian behavior is pseudoplastic, or shear thinning behavior (i.e., viscosity decrease with increasing shear rates).

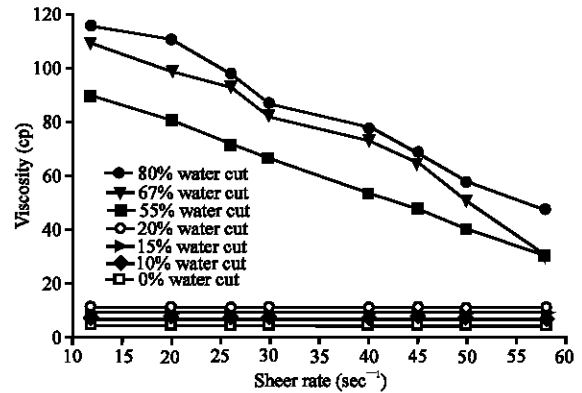


Fig. 1: Viscosity vs. shear rate of crude oil emulsions

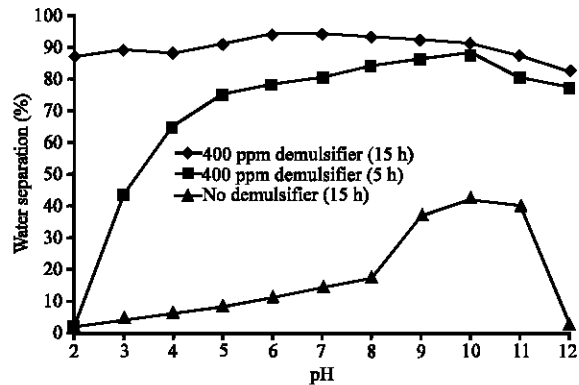


Fig 2: Effect of pH and demulsifier concentration on emulsion stability

pH: Water-phase pH has a strong influence on emulsion stability (Kimbler *et al.*, 1966; Strassner, 1968; Jones *et al.*, 1978). The stabilizing, rigid-emulsion film contains organic acids and bases, asphaltenes with ionizable groups and solids. The pH of water affects the rigidity of the interfacial films. pH also influence the type of emulsion formed. Low pH (acidic), generally produces w/o emulsions, whereas high pH (basic) produces o/w emulsion. Figure 2 shows the effect of pH on emulsion stability. The optimum pH for demulsification is found at 10 without demulsifier. Addition of a demulsifier enhances demulsification after 5 h and the maximum water separation (95% v/v) is achieved after 15 h.

Interfacial Pressure (Ω): The interfacial pressure of demulsification process (Ω) is defined as the difference between the interfacial tension of the oil containing stabilizer/aqueous phase γ_o and that of the same system when a destabilizer γ_d is added. The interfacial pressure Ω is calculated from equation $\Omega = \gamma_o - \gamma_d$, where γ_o and γ_d are the interfacial tension between crude oil and synthetic oil field emulsion before and after addition of demulsifier, respectively. Results of this study showed that the higher (Ω) value, the higher the instability of emulsion and vice

versa. The interfacial pressure of various demulsifiers related to the percentage of water and oil separation is presented in Table 3. As shown in the Table 3, there is a direct correlation between the interfacial pressure and the percentage of water separation.

Based on the results, the demulsifiers can be divided into three groups. The first group consists of the demulsifiers such as amine group, sulphonate and polyhydric alcohols group which have Ω values ranging from 4.1 to 7.5 which can destabilize the emulsion. The amount of water which can be separated from the emulsion is up to 80%. The second group comprises Polyethylene Glycol (PEG) 600, Polyethylene Glycol (PEG) 1000, AOT, propylamine which have Ω values ranging from 2 to 6 and can partly break the emulsion. The amount of water separated from this group is in the interval of 25 to 67%. The third group consists of poly PO terminated, polyethylene block PEG, polyethylene Oxide (PEO), 100000, trioctylamine, Propylene glycol, PG, ethylene glycol, EG and NaDBS which have Ω values ranging from -8 to 2.8 and could not destabilize the emulsion. The percentage of water separation is less than 15%.

Figure 3 and 4 shows some typical results of demulsification experiments conducted to test the

Table 4: The influence of butanol in enhancing the destabilization process of cru-de oil using oil soluble demulsifiers

Demulsifier	Concentration (mole L ⁻¹)	Water separation (%) (v/v)		Oil separation (%) (v/v)	
		Without butanol	With butanol	Without butanol	With butanol
Diocetylamine	0.2485	43	48	58	66
Igepal	0.0024	22	54	53	60
AOT	0.0013	38	47	68	74

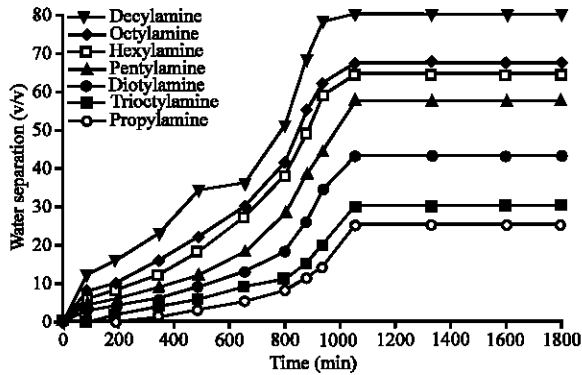


Fig. 3: The influence of amine group demulsifiers on crude oil emulsion stability (percentage of water separation)

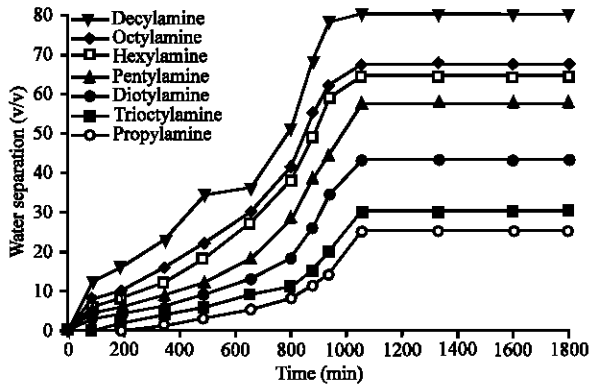


Fig. 4: The influence of amine group demulsifiers on crude oil emulsion stability (percentage of oil separation)

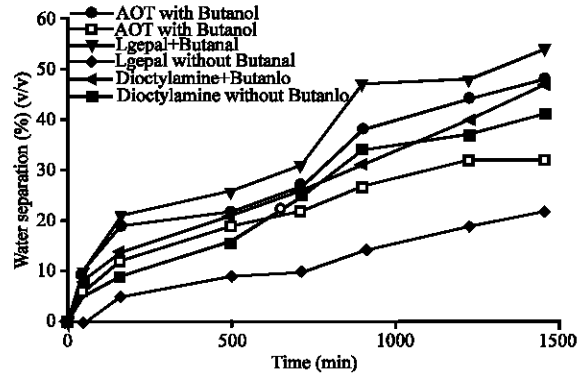


Fig. 5: The influence of butanol in enhancing the oil soluble demulsifiers respect to water separation

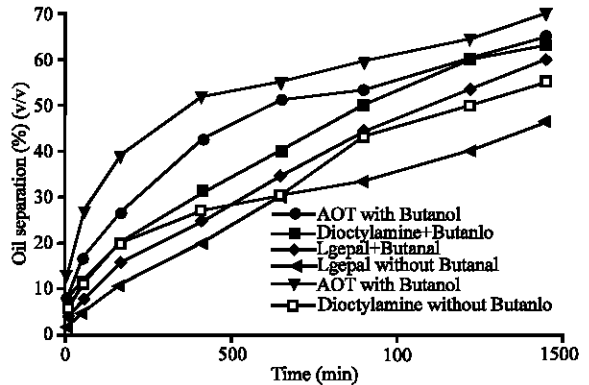


Fig. 6: The influence of butanol in enhancing the oil soluble demulsifiers respect to oil separation

influence and performance of the amine group demulsifiers on the crude oil emulsion stability. Figure 3 and 4 shows separation of water and oil from water-in-oil emulsions as a function of time, respectively. As shown in Fig. 3 and 4, all amine groups showed the water and oil separations. This could be attributed to a very specific interaction between the amine added and the naturally occurring constituents in the interfacial film.

The large agglomerates have a larger sedimentation velocity than the individual particles and require larger forces to hold them at the interface. The equation for sedimentation velocity from Stoke's law is:

$$v_w = \frac{2R^2(\rho_w - \rho_o)g}{9\mu_o} \quad (2)$$

where; v_w is the sedimentation velocity, R is the water droplets radius; ρ_w , ρ_o are the densities of water and oil, respectively; g is the force acting on the system (gravitational) and μ_o is the viscosity of the continuous (oil). As droplets agglomerate, the density flocs decreases because of entrained continuous phase (oil), but their radius increases, resulting in a higher sedimentation velocity because of the squared dependency on the radius.

Effect of Alcohol Addition on Demulsification Performance

Oil soluble demulsifier: To study the effect of alcohol addition on demulsification performance, this study used three oil soluble demulsifiers; dioctylamine, igepal and aerosol T (AOT) Table 4.

Figure 5 and 6 shows the profiles of water and oil separation from emulsion destabilized by the oil soluble demulsifiers alone as well as adding butanol as enhancement agent. As shown in Figure 5 and 6, the performance of all demulsifiers either water or oil separation can be enhanced by adding alcohol. In general, after 1440 min, the percentage of water separation without adding butanol alcohol is less than 43%. In contrast, destabilization process by adding butanol can improve the water separation ranging from 43 to 48 for dioctylamine, 22 to 54 for igepal and 38 to 47% for AOT, respectively. Our experimental results showed that using butanol alone there were no emulsion destabilization for 24 h, these percentages of separation are smaller than other demulsifiers. It means that butanol does not effect the destabilization if used alone as destabilizer, but they can enhance the destabilization process when used together with a demulsifier. Butanol is grouped into medium chain alcohol that possesses the solubility properties, like slightly soluble in water and more soluble in non-polar or weakly polar compound. It is different from low chain alcohol (C1-C3) which is miscible in water, or long chain alcohol (C7 or more) to be insoluble in water. Dioctylamine is non-polar compound that is not soluble in water because the highly polar water molecules are held to each other by very strong dipole-dipole interaction hydrogen bonds. It's a very weak attractive force between water molecules and the non-polar dioctylamine molecules.

The influence of butanol in enhancing the AOT demulsifier performance shows that the percentage of water separation is less than the oil separation at any time. For example, for 1440 min both percentages of water and oil separation from the emulsion are 47 and 74%, respectively.

CONCLUSIONS

Based on results of this study, it can be concluded that, emulsions are characterized by the type of emulsion (W/O or O/W), nature of emulsifying agents present, bulk viscosity and interfacial viscosity. The percentage of water separated is the best indicator of emulsion stability, because it is a measure of the degree of aggregation or flocculation of individual emulsion water droplets and coalescence of aggregated water droplets. Water phase pH it found has a strong influence on emulsion stability.

Four chemical demulsifiers were used to perform demulsification tests. These chemicals were; amine groups, polymeric, sulphonate and polyhydric alcohol demulsifiers. Three oil soluble demulsifiers blended with alcohol and thoroughly investigated their effect on demulsification performance.

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