DEMULSIFIER SELECTION BASED ON THE EVALUATION OF DEMULSIFICATION PERFORMANCE INDICATORS

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Abstract

A method for characterizing and selecting demulsifiers has been developed. The development was based on either the relationships between the demulsification parameters and demulsifier performance or demulsifier characteristics and demulsifier performance. The importance of each of these parameters to performance was discussed. The result was eight demulsification performance indicators consisting of the percentage of water separation, percentage of oil separation, demulsification efficiency, demulsifier effectiveness, partition coefficient, interfacial pressure, interfacial activity, and Hydrophilic Lipophilic Balance (HLB). Quantification of the indicators conducted by determination of the performance indexes for each indicator. It was obtained from the condition that the demulsifier exhibits good performance. Additionally, the study found a correlation between the parameters itself. The demulsifier effectiveness as well as the interfacial pressure reaches a maximum value when the partition coefficient closed unity. Increasing of the interfacial pressure, in consequence, will increase both the demulsifier effectiveness and interfacial activity. The effect of both the HLB and molecular weight on the percentage of separation indicates a weak correlation.

Key words: *Chemical demulsification, demulsifier performance, demulsification parameters, performance index.*

1. Introduction

Many problems that related to chemical demulsification of crude oil emulsion are necessary to be discussed. One of the problems is how to develop a method for selecting the demulsifier related to either the parameter of demulsification or demulsifier characteristics. Recently, the selection of a demulsifier in commercial application is based on trial and error process (Zaki *et al*, 1996). As the nature and stability of petroleum emulsion vary from field to field, horizon to horizon and even from well to well, the same demulsifier may not be useful for the breaking of all the crude emulsion (Sharma *et al*, 1982). In fact, there is no unique physicochemical parameter, which can be correlated completely with crude oil emulsion stability (Thompson *et al*, 1985), so a complete knowledge of how the demulsifiers destabilize the naturally occurring emulsion is not clear [4]. The selection of a demulsifier is rather complicated, and requires cooperative testing between the user and the demulsifier manufacturer. The selection of a demulsifier depends on the properties of the system and on the desired process or product improvement. Thus, the physical and chemical conditions needed to sustain their activity must be discussed and made available to both the user and the demulsifier manufacturer. Subsequently, a detailed methodology for selecting the demulsifier does not exist because of the diversity of surface activities and the widely varying industrial applications of demulsifiers (Kouloheris, 1989).

A method for selection of demulsifier is based on the solubility either in water or oil. The water-soluble emulsifiers tend to give the o/w emulsion and oil soluble emulsifiers give the w/o emulsion. This concept is known as Bancroft's rule. The destabilization of w/o emulsions can be achieved by the addition of surface-active agents, which promote o/w emulsions. It means that water-soluble surfactants are more capable of stabilizing o/w emulsions and vice versa (Zaki *et al*, 1996; Urdahl *et al*, 1993). The methods used above are entirely qualitative. Hydrophilic-Lipophilic Balance (HLB) is quantitative method, which is more useful for choosing a suitable surfactant either for emulsifier or demulsifier agent (Zaki *et al*, 1996; Cooper *et al*, 1980; Dai *et al*, 1997; Boyd *et al*, 1972; Cavallo, 1990; Kloet *et al*, 2002, Al-Sabagh, 2002). HLB is an empirical scale, which was originally developed in studies of emulsification (Becher, 1955). A Method for selecting the demulsifier has been developed. It involved a consideration of the surface and structural chemistry of the demulsifier molecule (Berger *et al*, 1988). Many researchers had investigated the performance parameters of demulsifier such as interfacial pressure (Sjoblom *et al*, 1992; Sjoblom *et al*, 1995; Bhardwaj and Hartland, 1994), interfacial activity (Berger *et al*, 1988; Krawczyk *et al*, 1991; Kim *et al*, 1995; Kim and Wasan, 1996; Radzio and Prochaska, 2001; Standal *et*

al, 1999), partition coefficient (Berger et al, 1988; Krawczyk et al, 1991; Kim and Wasan, 1996; Standal et al, 1999; Caldero et al, 1997; Reinsel et al, 1994), demulsifier effectiveness (Krawczyk, 1990), and chemical demulsification efficiency (Sharma et al, 1982). However, no investigators studied the all demulsifier parameters. Most of studies elucidated the idea for a little parameter by using the composite demulsifiers. Investigations about the relationship between the whole parameters are relatively scanty. In order to carry out the demulsifier screening and selecting process successfully, a complete knowledge of the relationship between the demulsification parameters and destabilisation process is important.

This experiment consists of many steps. The first step involves the demulsifier performance evaluation using various single demulsifiers from both the oil-soluble and water-soluble demulsifiers. The second step is the study on demulsifier performance parameters consists of both the demulsification parameters and demulsifier characteristics. The final step is making a correlation either between the first and second step or between the parameters itself.

2. Experimental
2.1. Materials
Crude oil sample (COE1) was obtained from the Malaysian oil field. The synthetic oilfield brine used in this experiment was prepared by dissolving NaCl in double distilled water to obtain the solution with salinity of $9.4^0/_{00}$ which is equivalent to the salinity of the oilfield brine sample of COE1. The chemicals used for experiment were the reagent grade octylamine (98.0%, from Fluka), dioctylamine (97.0%, Fluka), trioctylamine (95%, Fluka), hexylamine (98.0%, Fluka), tetraethylenepentamine (85,0%, Fluka), ethylene glycol (99.5%, Fluka), propylene glycol (99.5%, Fluka), polyethylene glycol (PEG) 600 (99.5%, Fluka), polyethylene glycol (PEG) 1000 (Fluka), nonyl phenol (99.0%, Fluka), dodecyl phenol (99.0%, Aldrich), igepal CA 630 (99%, Fluka), polypropyleneoxide terminated (Aldrich), aerosol OT (99%, Sigma), dodecyl benzene sulphonic acid (90.0%, Fluka), methyltrioctyl ammonium chloride (90.0%, Merck), tetraoctyl ammonium bromide (Sigma), and sodium chloride (99.8%, Merck). All chemicals were used without further purification.

2.2. Surface and interfacial tension measurement.
The surface tension and interfacial tension either the organic or aqueous phase of crude oil emulsions were determined by using Kruss Digital Tensiometer K 10 ST with a water bath thermostat. The measurement used the plate method. The surface tension or interfacial tension measurement was used to determine several demulsification parameters.

2.3. Chemical demulsification efficiency
The chemical demulsification efficiency (CDE) was calculated using Equation (1) as described by Sharma et al., 1982 [2].

$$CDE = \frac{x + 10x/y}{Q} \qquad (1)$$

where x is the percentage of water separated from emulsion; y is the percentage of water present in emulsion; Q is the quantity of demulsifier used in ppm.

2.4. Demulsifier effectiveness
The effectiveness of demulsifier is defined simply as the volume of water settled after 24 hours divided by the total volume of water present in the crude oil emulsion. For the synthetic oil emulsion system the settling time is usually taken 5 minutes (Krawczyk, 1990), due to the separation process of the emulsion is very quick, even final separation time is often reached less than 10 minutes. Different from the synthetic oil emulsion system, the real crude oil emulsion system is more stable. Generally, final separation time of this system is more than 5 days, many crude oils need a long time for breaking the emulsion completely.

2.5. Determination of the partition coefficient
The partition coefficient (K_P) is defined as the equilibrium ratio of the demulsifier concentration in the water phase (C_w) to the demulsifier concentration in the oil phase (C_o) [26]. Thus,

$$K_P = C_w/C_o \qquad (2)$$

The determination of the partition coefficient follows the procedure described by Krawczyk et al (1991). It requires a calibration plot of the interfacial tension of the oil phase (crude oil) containing known concentrations of the demulsifier against the synthetic oilfield brine (salinity $9.4^0/_{00}$). Equilibrated system was prepared by contacting the synthetic oilfield brine and the oil phase (COE1 crude oil) containing the demulsifier in a graduated cylinder under agitation at 300 rpm for 2 minutes. The initial concentration of each demulsifier in the oil phase was corresponded to the quantity of each demulsifier used. After 4 days, the equilibrated mixture in the graduated cylinder was centrifuged at 5000 rpm for 30 minutes. The two immiscible phases were separated, and the separated oil phase was used to determine the partition coefficient. The interfacial tension of the separated oil phase against the synthetic oilfield brine was measured by the Wilhelmy plate method. The concentration of the partitioned demulsifier in the separated oil phase (C_o) was determined by comparing the equilibrium interfacial tension measured against the calibration plot. The resulting mass balance allows the calculation of the partitioned demulsifier in the separated water phase (C_w), so that the partition

coefficient calculated. The measurement was carried out at least in triplicates and the average value was taken.

2.6. Interfacial pressure

The interfacial pressure of demulsification process (Π) 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 is added γ_d. Thus,

$$\Pi = \gamma_o - \gamma_d \qquad (3)$$

The interfacial tension (γ_o and γ_d) was determined by using Kruss Digital Tensiometer K 10 ST, following the procedure as described in Section 2.2.

2.7. Interfacial activity

Interfacial activity (α) is defined in Equation (4), which represents the slope of plot of interfacial tension as a function of demulsifier concentration.

$$\alpha = \frac{-\partial \gamma}{\partial \ln C} \qquad (4)$$

where γ is the static interfacial tension, and C is the bulk concentration of demulsifier. The variation of static interfacial activity with demulsifier concentration in the oil phase was determined from the interfacial tension isotherm. The interfacial tension as a function of demulsifier concentration was measured at room temperature (27 ^{o}C) using Wilhelmy plate method with using Kruss Digital Tensiometer K 10 ST.

2.8. Demulsifier performance test

All of the crude oil emulsions were prepared with equal proportions by volume of the aqueous and oil phase. The aqueous phase was the synthetic oilfield brine with salinity of 9.4^o/$_{oo}$. The oil phase was real crude oil of COE1. All emulsion was prepared by using Ultra Turrax T50 homogenizer with dispersing rod model S25N-25G, speed 8000 rpm for 80 seconds. The demulsification performance test was conducted by placing 10 ml of emulsion into a capped 20 ml graduated test tube. The demulsifier was added into each of test tubes and shaken for 60 seconds. The temperature during the destabilization test was kept at 30°C. The volumes of water and oil separated from the emulsion were recorded at specified time intervals. The measurement was carried out at least in triplicates and the standard deviation for the measurement was 0.08.

3. Results and Discussion

3.1. Demulsifier performance evaluation

The demulsifiers used in this experiment consist of both the oil soluble and the water- soluble demulsifiers. The performance of demulsifier can be understood by calculating either the percentage of water or oil separation from the emulsion.

3.1.1. Oil soluble demulsifier

Table 1 shows the performance of the oil-soluble demulsifier in destabilizing water-in-oil emulsion. The oil soluble demulsifiers involve a non-ionic group such as amines (hexylamine, octylamine, dioctylamine, trioctylamine) and phenolic (nonyl phenol, dodecyl phenol, igepal) compounds, cationic group such as quaternary ammonium salts (TOMAC, TOAB), and anionic group (AOT).

Table 1 The performance of oil soluble demulsifier in destabilizing water-in-oil emulsion

Demulsifier	Concentration (mole/l)	Water separation (% vol.)		Oil separation (% vol.)	
		24 hours	48 hours	24 hours	48 hours
Hexylamine	0.2485	74	78	80	80
Octylamine	0.2485	42	44	84	86
Dioctylamine	0.2485	34	34	96	96
Trioctylamine	0.2485	4	4	78	80
Nonyl phenol	0.2485	8	10	64	73
Dodecyl phenol	0.2485	0	0	35	50
Igepal	0.0024	8	24	54	60
AOT	0.0013	8	20	70	76
Methyltrioctyl Amm. Chloride (TOMAC)	0.0027	82	82	80	80
Tetraoctyl Amm. Bromide (TOAB)	0.0027	54	54	70	70

The percentages of water and oil separation were observed within 24 and 48 hours. In general, all demulsifiers are capable to separate either the oil or water from an emulsion, with an exception for dodecyl phenol, trioctylamine, and nonyl phenol which can only separate the water for none, 4%, and 10% respectively. After 48 hours, the percentage of oil separated was ranging from 50% to 96%, while for the water separated was ranging from 20% to 82%. TOMAC shows the best performance, followed by amines, sulphonate, and phenolic compound, respectively. In regard to demulsifying ability, the order is as follows: Hexylamine > Octylamine > Dioctylamine > Trioctylamine. In other word the order of amine compounds in separating water from the emulsion were primary amine > secondary amine > tertiary amine. Based on the solubility of amines in water, octylamine, dioctylamine, and trioctylamine are insoluble in water while hexylamine is slightly soluble in water due to its hydrophobic chain is shorter than that of octylamine. Subsequently, according to the result presented in Table 1, hexylamine has higher capability to separate water than octylamine, dioctylamine or trioctylamine do. However, hexylamine and octylamine are primary amines, but hexylamine is better than octylamine because hexylamine has hydrophobic chain shorter than octylamine, so it is more soluble in aqueous phase. Similar results were also reported by Sjoblom *et al.* (1990) in their study on the effect of different chemical additives on crude oil emulsion stability (Sjoblom *et al*, 1990).

Both TOMAC and TOAB are able to destabilize the crude oil emulsion either to separate the water or oil, but TOMAC is better than TOAB. Most quaternary ammonium salts are especially valuable because they are somewhat soluble in both water and nonpolar organic solvents. The chemical structure of both TOMAC and TOAB are similar. TOMAC is formed from the starting material trioctylamine, which is reacted with methyl chloride, so that the hydrophobic group consists of three octyl chains, one methyl chain with a positive charge, and an ion chloride with a negative charge. TOAB has hydrophobic group that consists of four octyl chains, which have positive charge, and an ion bromide with a negative charge. Based on the contents of hydrophobic long-chain, the following can be predicted: (1) TOMAC and TOAB are dispersible in water and soluble in organic solvents because they have more two hydrophobic long alkyl chains; (2) TOMAC is less hydrophobic than TOAB, so it is able to reach the water-oil interface.

Nonyl phenol, dodecyl phenol, and igepal CO-630 are grouped into phenolic group demulsifier. Based on the demulsifying ability, the order is as follows: igepal >nonyl phenol> dodecyl phenol. This may be related to the molecular structure of the agent. Nonyl phenol contains both nonyl (C9) chain and unsaturated carbon ring as hydrophobes and hydroxyl group as hydrophile. Dodecyl phenol has the same structure as nonyl phenol with exception that it contains dodecyl (C12) chain as hydrophobe. Igepal CO 630 is nonyl phenol ethoxylated with 9 moles of ethylene oxide (EO). It has both nonyl (C9) chain and unsaturated carbon ring as hydrophobes beside of hydroxyl group and EO group as hydrophile. The addition of EO (ethoxylation) into alkyl phenol compound is meant to increase both hydrophilic portion and the HLB number. In consequence its solubility in aqueous phase increases. In other words, the molecule of Igepal is more partitioned to the water droplet phase, so that the demulsifying performance is improved. Based on the hydrophobe chain length, nonyl phenol contains hydrophobe tail shorter than dodecyl phenol does. Igepal has the same hydrophobe tail as nonyl phenol, but it has longer hydrophile head. Subsequently, in regard to the length of hydrophobic tail the structure of nonyl phenol and igepal cannot be as tightly packed in interfacial layer as those of dodecyl phenol.

3.1.2. Water-soluble demulsifier

Table 2 shows a performance of the water-soluble demulsifier in destabilizing water-in-oil emulsion. The water-soluble demulsifiers involve a non-ionic group such as amine (tetraethylenepentamine), polyhydric alcohol (ethylene glycol, propylene glycol, PEG 600, PEG 1000), polymeric (polyethylene oxide, poly propylene oxide terminated) compound; and anionic group (DBSA). The percentages of water and oil separation were observed within 24 and 48 hours. In general, all demulsifiers are weak in separating either water or oil from the emulsion with the exception for both Poly PO terminated and DBSA which can separate 70% and 80% of the oil. The other demulsifiers can only separate oil lower than 50%, and water lower than 12%, with the exception PEG 1000 which can separate water up to 43%. Even, after 48 hours, propylene glycol, tetraethylenepentamine, poly PO terminated, and polyethylene oxide 1,000,000 cannot separate water from the emulsion.

Based on the result, one may conclude that the oil soluble demulsifier is preferred in separating either water or oil from water-in-oil emulsion than the water-soluble demulsifier. However, oil soluble demulsifier is relatively good for oil separation. In contrast, the water-soluble demulsifiers are not capable in separating water from the same emulsion.

Table 2 The performance of water soluble demulsifier in destabilizing water-in-oil emulsion

Demulsifier	Concentration (mole/l)	Water separation (% vol.)		Oil separation (% vol.)	
		24 hours	48 hours	24 hours	48 hours
Ethylene glycol	0.2485	2	2	24	26
Propylene glycol	0.2485	0	0	22	24
PEG 600	0.2485	10	10	48	56
PEG 1000	0.2485	43	43	32	42
Tetraethylenepentamine	0.2485	0	0	28	42
Poly PO terminated	800 ppm	0	0	64	70
Polyethyleneoxide 600,000	600 ppm	12	12	24	26
Polyethyleneoxide 1,000,000	1000 ppm	0	0	22	30
Dodecyl Benzene Sulphonic Acid (DBSA)	0.0013	8	8	78	80

3.2. Demulsifier performance indicators and correlation between parameters

The results of demulsifier performance evaluation are obtained in term of the percentage of water and oil separation from the emulsion. Further, it is necessary to discuss the demulsifier performance indicators in order to obtain a correlation between the separation process performance and demulsification parameters. Demulsifier performance indicators are parameters obtained from both the demulsification physicochemical characteristic and demulsifier characteristics as indicators. Demulsification physicochemical as indicators include the parameters such as chemical demulsification efficiency, effectiveness demulsifier, partition coefficient, interfacial pressure, and interfacial activity; while the demulsifier characteristic as indicators include the hydrophilic-lipophilic balance (HLB), molecular weight, and chemical structure and properties. The relationship between the demulsifier performance indicators and the percentage of water/oil separation for various demulsifiers (oil soluble and water soluble demulsifier) is presented in Table 3. This table shows the difference between the oil-soluble and water-soluble demulsifiers, clearly. The oil-soluble demulsifiers have the partition coefficients more than unity, whereas those of the water-soluble demulsifiers are less than unity. The partition coefficient lower from unity implies that it is more soluble in oil. In contrast, the higher value from unity denotes that it is more soluble in water. In addition, there exists a strong correlation between interfacial pressure as well as interfacial activity and the percentage of water/oil separation. If both the interfacial pressure and interfacial activity are large, the percentage of water separation as well as the percentage of oil separation is large, too (more than 70%). In contrast, when both parameters are small, the percentage of water separation is small, too. Negative value of interfacial pressure implies that the water separation is difficult. The higher interfacial activity, the more water and oil separated. The oil soluble demulsifiers perform interfacial pressure higher than the water-soluble demulsifiers do. The same case also performed for the interfacial activity. There exists a strong correlation between the interfacial activity and demulsifier effectiveness. High demulsifier effectiveness is obtained when the interfacial activity is high, either the oil soluble or water-soluble demulsifier. For example, hexylamine, TOMAC, TOAB, and PEG 1,000 have a high value of both interfacial activity and demulsifier effectiveness. In contrast, low interfacial activity will give low demulsifier effectiveness. The effect of both HLB and molecular weight on the percentage of separation indicates a weak correlation. Based on the discussion above, one may conclude that the oil soluble demulsifiers are better than the water-soluble demulsifier in destabilizing water in oil emulsion.

3.3. Demulsification performance index

In order to select the demulsifier, it is necessary to determine an index or minimum value of each indicator called *Demulsification Performance Index*. Table 3 exhibits that a demulsifier with a partition coefficient close to unity has a better performance.

For example, the oil-soluble demulsifier from amines group and TOMAC with the partition coefficient ranging from 0.2857 to 0.9490 give a better percentage of water and oil separation. The percentage of oil and water separation reaches 96% and 82%, respectively. In contrast, the water-soluble demulsifiers having large partition coefficients (more than 100) give a bad performance on water or oil separation.

Table 3 Demulsification Performance Indicators of various demulsifiers

No.	Demulsifier	Percent of Separation within 48 hours (% vol.)		Chemical Demulsification Efficiency	Demulsifier Effectiveness, ε	Partition Coeff. K_p	Interfacial Pressure, π (mN/m)	Interfacial Activity, α (mN/m)	HLB	Molecular Weight
		Water	Oil							
	Oil soluble									
1.	Hexylamine	78	80	0.00363	0.74	0.9490	12.7	16.45	6.98	101.19
2.	Octylamine	44	86	0.00164	0.42	0.7138	12.0	12.08	6.88	129.25
3.	Dioctylamine	34	96	0.00068	0.34	0.5061	1.1	12.54	6.75	241.46
4.	Trioctylamine	4	80	0.00005	0.04	0.3432	-8.2	5.62	5.00	353.68
5.	TOMAC	82	80	0.08245	0.82	0.2857	12.9	54.28	6.55	442
6.	TOAB	54	70	0.04389	0.54	0.1250	1.7	22.33	6.25	546.8
7.	AOT	20	76	0.04152	0.08	0.6250	11.3	18.18	13.65	444.6
8.	Nonyl Phenol	10	73	0.00021	0.08	0.0757	5.0	13.42	2.7	220.36
9.	Dodecyl Phenol	0	50	0.00000	0.00	0.1044	3.2	8.69	1.3	262
10.	Igepal	24	61	0.01924	0.08	0.2150	10.5	16.06	13	616
	Water soluble									
11.	DBSA	8	80	0.02262	0.08	2.7143	-0.4	9.23	7.35	326.5
12.	TEP	0	42	0.00000	0.00	247	3.4	2.57	8.98	189.31
13.	Ethylene Glycol	2	26	0.00016	0.02	9939	2.2	6.35	9.85	62.07
14.	Propylene Glycol	0	24	0.00000	0.00	7099	0.6	5.08	9.4	76.1
15.	PEG 600	10	56	0.00008	0.10	28.20	3.4	3.12	13.2	600
16.	PEG 1,000	43	42	0.00021	0.43	198	4.5	25.47	16.2	1000
17.	PEO 600,000	12	26	0.02400	0.00	153	-3.7	7.65	8.80	600,000
18.	PEO 1,000,000	0	30	0.00000	0.00	166	-1.7	7.22	8.83	1,000,000
19.	Poly PO term.	0	70	0.00000	0.00	2.4783	2.8	6.09	7.32	-

A demulsifier with interfacial pressure more than 11 mN/m and interfacial activity ≥ 16 mN/m, demulsifier effectiveness ≥ ..., K_p of 400-600 (for ... and 600-1000 (for water soluble demulsifier) will give good separation.

Based on the literature study and the experimental results related to the demulsifier performance, ... performance index ... performance index proposed is listed in Table 4. A demulsifier is in a good category when the values of demulsification performance indicators are more than the performance index.

2.4 Demulsifier Selection

Demulsifier selection is carried out as follows:

The first step is to calculate demulsifier performance indicators of each demulsifier.

Fulfillment the performance index ...

A good demulsifier is obtained when all of indicators fulfill the performance index. From screening the indicators the demulsifier with good performance can be selected based on the concentration. The demulsifier, hexylamine, TOMAC, and AOT are selected. Furthermore, the three demulsifiers are compared in each other to get the best one.

As mentioned earlier, ... performance test of hexylamine, AOT, ... use different concentration in order to obtain best performance. The concentration utilized in the experiment for hexylamine, AOT, and TOMAC are ... 2.2485 ... and 0.0027 mole/l, respectively. The three demulsifiers may be compared by using the same concentration at different level. The concentration level is 0.005 mole/l, 0.010 mole/l, and ... 0.050 mole/l.

Figure 1 ... water separation from emulsion using hexylamine, AOT, and TOMAC demulsifiers at various concentration levels. Figure 1a shows the rate of water separation at concentration level of demulsifier 0.005 mole/l. After 2800 minutes ... TOMAC ... water from the emulsion, while using hexylamine or AOT there is no water separation at the time. As the demulsifier concentration is increased to 0.010 mole/l, as presented in Figure 1b, the percentage separation for ... AOT and no water separation for ... demulsifier of 0.05 mole/l as shown in Figure 1c, TOMAC can separate water from the emulsion completely, while both AOT and hexylamine remain constant ...

Table 4 Demulsifier Performance Index

No	Demulsification Performance Indicator	Demulsification Performance Index
1	Percent of Water Separation (within 48 h)	$\geq$ 70 %
2	Percent of Oil Separation (within 48 h)	$\geq$ 70 %
3	Chemical Demulsification Efficiency (48 h)	> 0.04
4	Demulsifier Effectiveness (within 24 h)	$\geq$ 0.30
5	Partition Coefficient (K_p)	$0.2 < K_p < 1.8$
6	Interfacial Pressure (Π)	> 11 mN/m
7	Interfacial Activity (α)	> 16 mN/m
8	HLB (for breaking W/O emulsion)	6.5 -18
	HLB (for breaking O/W emulsion)	3 - 6
9	Molecular Weight	
	Oil soluble demulsifier	400 – 600
	Water soluble demulsifier	600 - 1000
10	Chemical Structure & Properties	
	(for breaking W/O emulsion)	Oil soluble demulsifier
	(for breaking O/W emulsion)	Water soluble demulsifier

A demulsifier with interfacial pressure more than 11 mN/m, interfacial activity > 16 mN/m, demulsifier effectiveness > 0.30, and molecular weight of 400-600 (for oil soluble) and 600-1000 (for water soluble demulsifier) will give a good separation.

Based on the literature study and the experimental result related to the demulsification performance, the present study proposes the performance index for each indicator. The performance index proposed is listed in Table 4. A demulsifier is in a good category when the values of demulsification performance indicators are more then the performance index.

3.4. Demulsifier selection

Demulsifier selection is carried out as follows: The first step is to select the Demulsifier Performance Indicators of each demulsifiers (Table 4) which fulfillment the Performance index as listed in Table 4. A good demulsifier is obtained when all of indicators fulfill the Performance index. From screening the indicators the demulsifiers with good performance can be selected. Based on the criteria above, three demulsifier, hexylamine, TOMAC, and AOT are selected. Furthermore, the three demulsifiers are compared in each other to get the best one.

As mentioned in Table 1 the demulsification performance test of hexylamine, AOT, and TOMAC use different concentration in order to obtain best performance. The concentration utilized in the experiment for hexylamine, AOT, and TOMAC are 0.2485 mole/l, 0.0013 mole/l, and 0.0027 mole/l, respectively. The three demulsifiers may be compared by using the same concentration at different level. The concentration level is 0.005 mole/l, 0.010 mole/l, and 0.050 mole/l.

Figure 1 shows rate of water separation from emulsion using hexylamine, AOT, and TOMAC demulsifiers at various concentration levels. Figure 1a shows the rate of water separation at concentration level of demulsifier 0.005 mole/l. After 2800 minutes TOMAC can separate 64% of water from the emulsion, while using hexylamine or AOT there is no water separation at the time. As the demulsifiers concentration is increased to 0.010 mole/l, as presented in Figure 1b, the percentage separation for TOMAC becomes 96%, 40% for AOT and no water separation for hexylamine. At concentration level demulsifier of 0.05 mole/l as shown in Figure 1c, TOMAC can separate water from the emulsion completely, while both AOT and hexylamine remain constant.
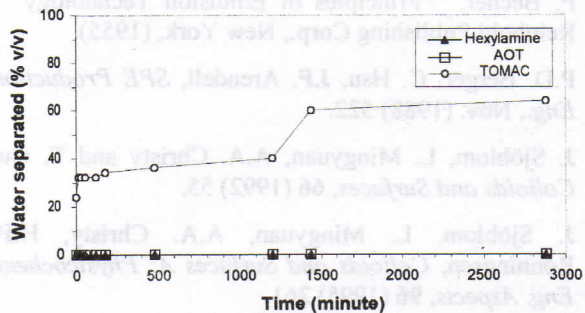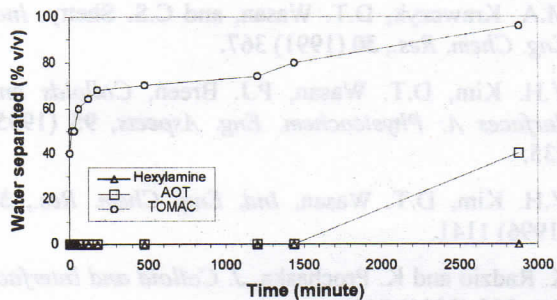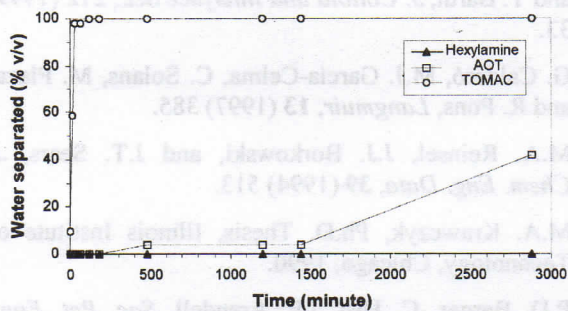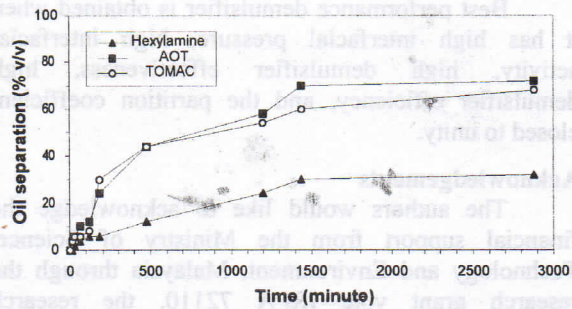
Figure 1a

Figure 1b

Figure 1c

Figure 1 Separation of Water from the emulsion using for various demulsifiers at different concentration: (a) 0.005 mole/l; (b) 0.01 mole/l; and (c) 0.05 mole/l.

Figures 2 shows the rate of oil separation from emulsion using hexylamine, AOT, and TOMAC demulsifiers at various concentration levels of 0.005 mole/l, 0.010 mole/l, and 0.05 mole/l, respectively. Similar to Figure 1, as the demulsifiers concentration increases the percentage of oil separation increases, too. At concentration of 0.005 mole/l (Fig 2a), the percentage of oil separated by using AOT is higher than that by TOMAC at any time. After 2800 minutes AOT can separate 72 % of oil from the emulsion while TOMAC can separate 70 % only. In this condition hexylamine can only separate 32 % of oil from the emulsion. At concentration 0.01 mole/l and 0.05 mole/l, the oil can be separated by TOMAC more than AOT as well as hexylamine.
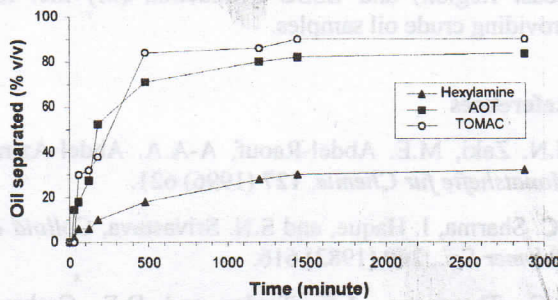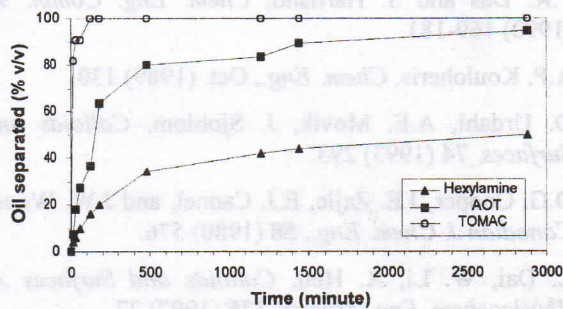

Figure 2a

Figure 2b

Figure 2c

Figure 2 Separation of Oil from the emulsion using for various demulsifiers at different concentration: (a) 0.005 mole/l; (b) 0.01 mole/l; and (c) 0.05 mole/l.

4. Conclusion

Oil-soluble demulsifier is preferred in separating either water or oil from the water-in-oil emulsion than water-soluble demulsifiers. Oil-soluble demulsifier is relatively good for oil separation. In contrast, the water-soluble demulsifiers are not capable in separating water from the same emulsion.

The oil-soluble demulsifiers have the partition coefficient more than unity, whereas chose the water-soluble demulsifiers areis less than unity. The effect of both the HLB and molecular weight on the percentage of separation indicates a weak correlation. The demulsifier effectiveness as well as the interfacial pressure reaches a maximum value when the partition coefficient closed to unity. Increasing the interfacial pressure in consequence increases both the demulsifier effectiveness and interfacial activity.

Best performance demulsifier is obtained when it has high interfacial pressure, high interfacial activity, high demulsifier effectiveness, high demulsifier efficiency, and the partition coefficient closed to unity.

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