

Full Length Research Paper

Stability of water-in-crude oil emulsions: Effect of cocamide diethanolamine (DEA) and Span83

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Water-in-oil emulsions are important in the petroleum industry in production operations, where the water content of the emulsion can be as high as 60% in volume. An environmentally friendly, nonionic emulsifying agent for crude oil emulsions Cocamide diethanolamine (Cocamide DEA) is introduced in the present work. The emulsion formation, rheology, stability and water separation performance of the DEA emulsifier was tested and compared with the commercially known Span83 non-ionic emulsifier. Water content (30, 40 and 50 vol.%), emulsifier molecular weight, emulsifier concentration (0.5, 1.0 and 1.5 vol.%) were the major variables investigated. The formulated emulsions viscosities and shear stress were measured at different operating temperatures (28 to 90°C) and different spindle rotation speeds (50 to 200). The experimental results showed that, for all the emulsion formed, the viscosity of the emulsion increases by increasing the water content and emulsifier concentration and decreases by increasing the rotation speed. The viscosity measurements were not constant with the spindle speed which confirms the non-Newtonian nature of the formulated emulsions. Finally, the experimental results showed that the emulsions formulated using the DEA emulsifier were more stable than the Span83 emulsions where the water separation time was longer and the water separation percentage was lower.

Key words: Water in oil (w/o) emulsions, stability, surfactants, crude oil, diethanolamine (DEA).

INTRODUCTION

Span83 is a sesquiester of monooleate and dioleate at a 2:1 molar ratio and has an HLB of 3.7. It is commonly used in pharmaceuticals because of its low toxicity. Its structure is shown in Figure 1.

Sorbitan sesquiester Span83 are widely used in personal care products. Water in oil (w/o) emulsifier are particularly recommended for unsaturated lipid components such as oleyl alcohol or vegetable oils and serves as dispersing agents for insoluble liquids in other lipophilic liquids, used as wetting agents and dispersants for pigments in colour cosmetics and zinc oxide/titanium dioxide in sun care products. Cocamide diethanolamine (Cocamide DEA), a viscous liquid, made by reacting the mixture of fatty acids from coconut oils with diethanolamine is used as a foaming and emulsifying

agent to help thicken shampoo, body wash and facial cleansers. It offers no benefits to the skin.

The term "Emulsion" refers to the dispersion of one insoluble liquid phase into another liquid phase such as the dispersion of water in oil (w/o) or oil in water (o/w). At this situation, the resulting "liquid" is called "Emulsion". The dispersion of the first immiscible phase droplets into the other phase will increase the interfacial surface area and hence a greater interfacial free energy in the system (Guo et al., 2006). One of the early emulsion nature observations was conducted by Finga (1995) who characterized emulsions into three major categories namely, Stable, meso stable and unstable depending on the physical appearance, viscosity difference and elasticity. The stability of water-in-oil emulsions depends on the total structure of the molecular matrix of the interfacially active components. Size, aromaticity, types of carbonyl functionality and other functional groups in the bulk play an important role in the total stability of the

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emulsions (Guo et al., 2006). Naturally, crude oil emulsions are formed in the oil well with the presence of natural surfactants that forms a rigid interfacial film with high interfacial tension that prevents the dispersed phase droplets from coalescence and forming an independent phase that will separate.

The existence of the interracial active components in the crude oil such as the resins and the asphaltenes will control the stability of the interfacial film formed between the dispersed and continuous phases in the emulsions (Pekdemir et al., 2005; Sjöblom et al., 1994; Xia et al., 2004; Yang et al., 2005; Zhang et al., 2005a, b). This paper aims to investigate the effect of the environmentally friendly emulsifier cocamide DEA and Span83 on formulation and stability of w/o emulsions.

MATERIALS AND METHODS

Two types of non-ionic emulsifying agents were used in the present works which are Span83 and Cocamide (DEA). The DEA was used for the first time as an emulsifying agent for crude oil emulsions. The molecular weights of the DEA and the Span83 were 290 and 1175, respectively. The chemical structures of Span83 and DEA were shown in Figures 1 and 2, respectively. The addition concentration investigated for each emulsifier were 0.5, 1.0 and 1.5 vol. %.

Crude oil

The crude oil investigated in the present work is Miri-Tapis crude oil Blend collected from Kerteh, Malaysia. The characteristics of the used crude oil sample are presented in Table 1. The commercial crude oil sample is a blend of Miri heavy crude oil (70% by volume) and Tapis light crude oil (30% by volume). Initially, the crude oil investigated is homogenized and filtered to remove any solid contaminants.

Emulsion preparation

Figure 3 shows the flow diagram for the emulsion preparation procedure followed in the present work. A total of 18 emulsion samples were prepared which covers all the investigated variables in the present work (emulsifier type, emulsifier concentration and the water addition concentration).

The emulsion preparation procedure starts by choosing the emulsifier type (Span83 or DEA) with certain concentration (0.5, 1.0 or 1.5%). The emulsifier is dissolved in crude oil using electrical mixer. The mixing procedure was done with 1800 RPM mixing speed and for 15 min to ensure a complete dissolution of the emulsifier into the crude oil then and within the same agitation speed, de-ionized water is added slowly and continuously to the emulsifier-crude oil mixture to form Water-in-Crude oil emulsion. The water content (dispersed phase) addition percentage was 30, 40 and 50% by volume for the emulsions prepared. The resulting emulsion type was determined using water test tube method. In this method, a drop of each emulsion is added in a test tube containing water and was shaken gently. If the emulsion is W/O, the drop will remain as droplet since the oil continuous phase is unable to mix with the water in the test tube. If the emulsion prepared is O/W, the emulsion drop will spread out in the test tube.

Emulsion separation test

Gravity separation test was adopted in the present investigation to measure the stability of the formulated emulsions. The stability of each emulsion was determined by measuring the water separation. 100 ml of each sample was placed in a tested tube and left on the shelf for one week to measure the water separation rate. Measurements of the amount of water separated is recorded every one hour for the first 12 h then every two hours for the second 12 h.

Rheology tests

Emulsions viscosities, shear rate and shear stress measurements were carried out by Brookfield DV-C + cone/plate programmable viscometer using spindle 31 with a shear rate range of 0 to 1500 s⁻¹. The principle of operation of the DV-C+ is to drive a spindle which is immersed in the test fluid through a calibrated spring. The viscous drag of the fluid against the spindle is measured by the spring deflection. Spring deflection is measured with a rotary transducer and displayed according to either the CGS system or the SI system of units. Measurement of viscosity was performed within different operating temperature (28, 50, 70 and 90°C) and different rotation speeds (50, 100, 150 and 200 rpm). The variables interaction in the rheology test was factorial, that is, all the temperatures and rotation speeds were tested for each emulsion.

RESULTS AND DISCUSSION

Figures 4 and 5 show the effect of water content on the viscosities of the Span83 and DEA emulsions with addition concentration of 0.5% and at different temperatures and rotation speeds. The rest of the experimental data is tabulated in Table 2.

It is clear that the viscosity of the investigated emulsion increases by increasing the water cut within the addition percentage investigated (30, 40 and 50 vol%). Increasing the water content means increasing the dispersed phase interference (water phase) into the continuous phase (oil phase) and that will introduce a new complex body that consist of the dispersed water droplets in the oil phase with different apparent viscosity. It is well known that this relation is not always linear, that is the emulsion viscosity tends to increase by increasing the water content within the range of (0 to 50%) where the continuous phase (oil phase) still dominating and any further increase in the water content (60 to 90%) will result in possible phase inversion and a drastic drop in the viscosity values (Ilia et al., 2010; Abdurahman et al., 2008; Marco et al., 2005; Olav et al., 1997).

Figures 4 and 5 also highlight the effect of spindle rotation speed on the apparent emulsion viscosities. This test was conducted to evaluate the emulsion characteristics (Newtonian or non-Newtonian liquid). It is clear that for all the emulsions investigated, the viscosity relation with the rotation speed is not linear where the viscosity decreases by increasing the rotation speed of the spindle and that confirms that the resulting emulsions are non-Newtonian liquids. It is important to highlight that, at different rotation speeds, the viscosities

Table 1. Crude oil characteristics.

Density (g cm ⁻³)	0.778
Viscosity (cp)	14.64
Surface tension (mNm ⁻¹)	25.44
Interfacial tension (mNm ⁻¹)	22.60

Table 2. Viscosities and shear rate data for all the emulsions investigated.

Emulsifier	C (Vol.%)	Water cut (Vol.%)	Temperature (°C)	Speed (rpm)	Viscosity (Pa.s)	Shear stress	Emulsifier	C (Vol.%)	Water cut (Vol.%)	Temperature (°C)	Speed (rpm)	Viscosity (Pa.s)	Shear stress
Span83	1.0	50	28	50	326.5	57.7	DEA	1.0	50	28	50	398.30	50.4
				100	288.7	88.9					100	301.7	90.8
				150	192.2	92.4					150	297.8	96.8
				200	171.5	98.5					200	251.9	98.7
			50	50	166.2	27.6					50	209.3	35.8
				100	149.6	45.6					100	193.8	57.8
				150	125.8	62.5					150	171.7	78.1
				200	116.5	78					200	153.4	96.9
			70	50	80.1	11.8					70	120.7	22.7
				100	70.5	22.2					100	115.8	35.2
				150	67.8	31.2					150	105.3	48.1
				200	61.9	39.8					200	95.6	58.5
			90	50	58.2	6.65					90	71.4	14.7
				100	41.4	14.2					100	68.1	26.3
				150	39.5	20.4					150	64.2	35.7
				200	37.2	26.5					200	59.8	42.3
Span83	1.5	50	28	50	-	-	DEA	1.5	50	28	50	-	-
				100	-	-					100	-	-
				150	450.4	92.6					150	-	-
				200	390.7	96.4					200	401.7	99.5
			50	50	349.2	69.3					50	360.5	70.1
				100	278.7	85.6					100	225.3	88.9
				150	194.2	94.3					150	204.7	95.7
				200	192	95					200	199.3	99.4
			70	50	153.2	24.3					70	160.5	25.7
				100	118.4	37.4					100	120.7	40.7
				150	97.2	48.1					150	115.3	52.3

Table 2. Contd.

			200	89.6	56.5				200	101.7	60.4		
		90	50	87.1	15.9			90	50	92.4	16.4		
			100	75.3	25.4				100	80.9	29.4		
			150	65.8	32.7				150	77.3	42.7		
			200	58.3	39.4				200	65.2	59.3		
Span83		28	50	171.8	29.1				50	244.70	40.7		
			100	165.3	58.9			28	100	201.5	62.4		
			150	160.8	86.3				150	175.3	80.7		
			200	150.1	97.4				200	150.4	95.4		
		50	50	135.9	20.5			50	50	140.7	20.7		
			100	123.8	32.6				100	125.4	35.7		
	1	40	150	99.5	44.9	DEA	1	40	150	101.7	40.3		
			200	93.7	55.1				200	99.8	55.2		
		70	50	82.1	7.65			70	50	85.4	10.4		
			100	67.3	15.3				100	80.6	20.5		
			150	50.3	21.6				150	72.3	35.3		
			200	40.5	27.3				200	55.9	30.3		
		90	50	28.2	4.69			90	50	35.4	9.01		
			100	27	8.98				100	30.7	15.3		
			150	25.3	13.1				150	29.3	20.4		
			200	24.6	16.6				200	26.2	25.3		
Span83	1.5	40	28	50	189.9	43.2	DEA	1.5	40	28	50	268.00	45.9
				100	181.2	61.9					100	215	74.9
				150	172.6	88.2					150	195.6	82.5
				200	168.9	99.4					200	179.7	96.4
		50	50	160.9	20.5			50	50	160.2	27		
			100	154.3	42.7				100	129.6	44.3		
			150	145.3	55.7				150	113.2	57.5		
			200	123.7	60.2				200	103.9	69.6		
		70	50	96.4	8.91			70	50	91.8	14.9		
			100	78.3	16.7				100	82	24.8		
			150	60.3	20.5				150	75.4	33.2		
			200	45.8	30.3				200	72.3	41.4		

Table 2. Contd.

			90	50	34.8	5.73	50		90	50	54	9.08		
				100	30.2	10.81	100			100	49.5	16.8		
				150	28.7	15.3				150	47.6	22.8		
				200	26.3	19.8				200	41.1	27.9		
Span83	1	30	28	50	115	16.7		DEA	1	30	28	50	244.70	40.7
				100	106.3	30.8						100	201.5	62.4
				150	91.4	45.4						150	175.3	80.7
				200	90.7	60.1						200	150.4	95.4
			50	50	64.9	9.38				50	50	140.7	20.7	
				100	58.5	18.7					100	125.4	35.7	
				150	49.2	24.3					150	101.7	40.3	
				200	47.5	16.8					200	99.8	55.2	
			70	50	31.7	4.49				70	50	85.4	10.4	
				100	26.1	8.77					100	80.6	20.5	
				150	25.8	13.11					150	72.3	35.3	
				200	24.7	16.8					200	55.9	30.3	
			90	50	16.8	2.86				90	50	35.4	9.01	
				100	15.3	5.3					100	30.7	15.3	
				150	14.2	7.85					150	29.3	20.4	
				200	14.8	10.3					200	26.2	25.3	
Span83	1.5	30	28	50	123.7	19.2		DEA	1.5	30	28	50	200.00	33.8
				100	120.2	35.4						100	172.5	60.4
				150	117.9	48.9						150	159.6	74.3
				200	109.8	66.2						200	143.8	98.5
			50	50	70.4	9.79				50	50	132.5	15	
				100	65.5	19.3					100	106.8	27.9	
				150	60.9	27.4					150	89.5	38.5	
				200	53.4	34.9					200	83	48.1	
			70	50	40.7	5				70	50	75.9	12.5	
				100	31.2	9.79					100	66.4	20.2	
				150	29.4	13.8					150	60.2	29.7	
				200	26.8	18.2					200	55.4	32.7	
				50	20.5	3.72				90	50	40.1	9.1	
			90	100	17.7	6.54					100	39.2	15.8	
				150	16.2	8.97					150	37.3	20.4	
				200	15.9	12.7					200	36.5	25.3	

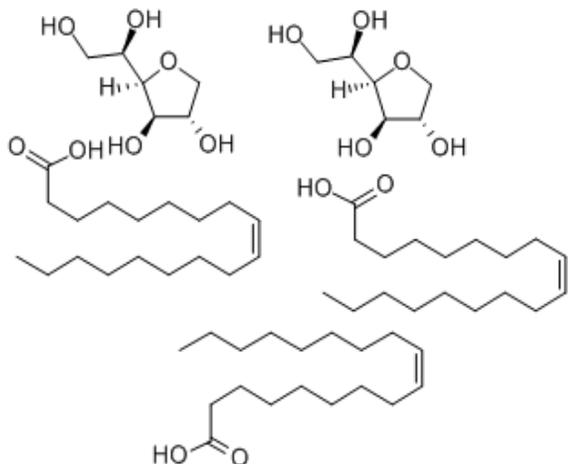


Figure 1. Chemical structure of Span83.

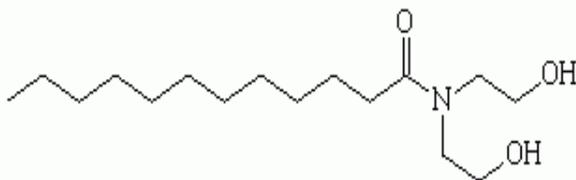


Figure 2. Chemical structure of cocamide DEA.

were close in value when the water content was 30 vol. % and the differences start to be higher by increasing the water content (Table 2). This highlights the effect of different operating parameters on the emulsions rheology such as the crude oil type and emulsifier type and their relation with the testing environment. It is believed that at 30% water content, the number water droplets dispersed in the oil phase was low and that will minimize the effect of spindle rotation speed (shear rate), while increasing the water content up to 50% will shift the (water-oil) status to form a tide emulsion that shows it non-Newtonian personality in a clear way.

One of the interesting findings of the present work is the effect of temperature on the emulsions viscosities. Figures 4 and 5 show that the emulsions viscosities decreases by increasing the testing temperature and the differences in the viscosities values start to be lower and the effect of spindle rotation speed is not as clear as in the results presented for lower temperatures. Increasing the temperature means increasing the internal movement of the water droplets dispersed in the oil continues media and that will increase the water droplets coalescence probability due to the reduction in the interfacial force between the water droplets and the oil media which will result in a weaker emulsion compared to the emulsions formed at lower temperatures. It is interesting to notice

that the effect of spindle speed reduces by increasing the testing temperature and that support the conclusion that increasing the temperature will result in a weaker emulsion that tends to act as a week Non-Newtonian liquid compared to the emulsion formed at 28°C but the emulsion still act as a non-Newtonian emulsion (Table 2).

Finally, by comparing the DEA and the Span83 emulsification performances, it is clear that both surfactants showed good ability to form a tight emulsion at room temperature (28°C). The DEA emulsifier emulsion viscosities for all the emulsions formed was higher compared with the Span83 and that is due to the very high molecular weight differences between the two surfactants. It is known that low molecular weight surfactants are highly effective in producing fine emulsions with a narrow size distribution due to their fast adsorption at the oil/water interface (Stang et al., 1994; Jixiang et al., 2006; McClements, 1999).

Figures 6 and 7 show the effect of shear rate on the apparent viscosity for selected data from the experimental tests conducted through the Brookfield rheometer while the rest of the data are listed in Table 2. Figure 6 shows the effect of the shear rate on the apparent viscosity of a 1.0% Span83 emulsion formed with 50% water cut and at different testing temperatures ranged between 28 to 90°C. It is clear that the apparent viscosity decreases by increasing the shear rate and also confirms the emulsions pursued pseudoplastic behavior. Such fact was confirmed in Figure 7 which shows the effect of the shear rate on the apparent viscosity of a 1.0% DEA emulsion formed with 50% water cut. For both figures, it is interesting to notice that the emulsion viscosity readings decreases by increasing the operation temperature which highlights a linear relation between the viscosity and the shear rate in the temperature range investigated.

A graphical comparison between the Span83 and the DEA shear rate-viscosity relation are present in Figure 8 while the rest of the data are tabulated in Table 2. Figure 8 shows the shear rate viruses and the apparent viscosity relation at 28°C for 40% water cut emulsion with 1% addition concentrations of Span83 and DEA. It is clear that the emulsion formed using the DEA shows higher apparent viscosity compared to the one formed using the Span83. What is important is that both emulsions showed non-Newtonian pseudoplastic behavior.

Figures 9 to 12 show the water separation tests results for the emulsions investigated using Span83 and DEA emulsifiers. Figures 9 and 10 highlight the effect of the emulsifier concentration on the water separation for the 50% water content emulsion. It can be noticed that the water separation reduces when the emulsifier concentration increases and that agrees well with most of the previously published works by many authors. A distinguishable water separation starts mostly after 6 h and reach almost a complete separation status after 168 h (7 days) for all the samples with maximum separation

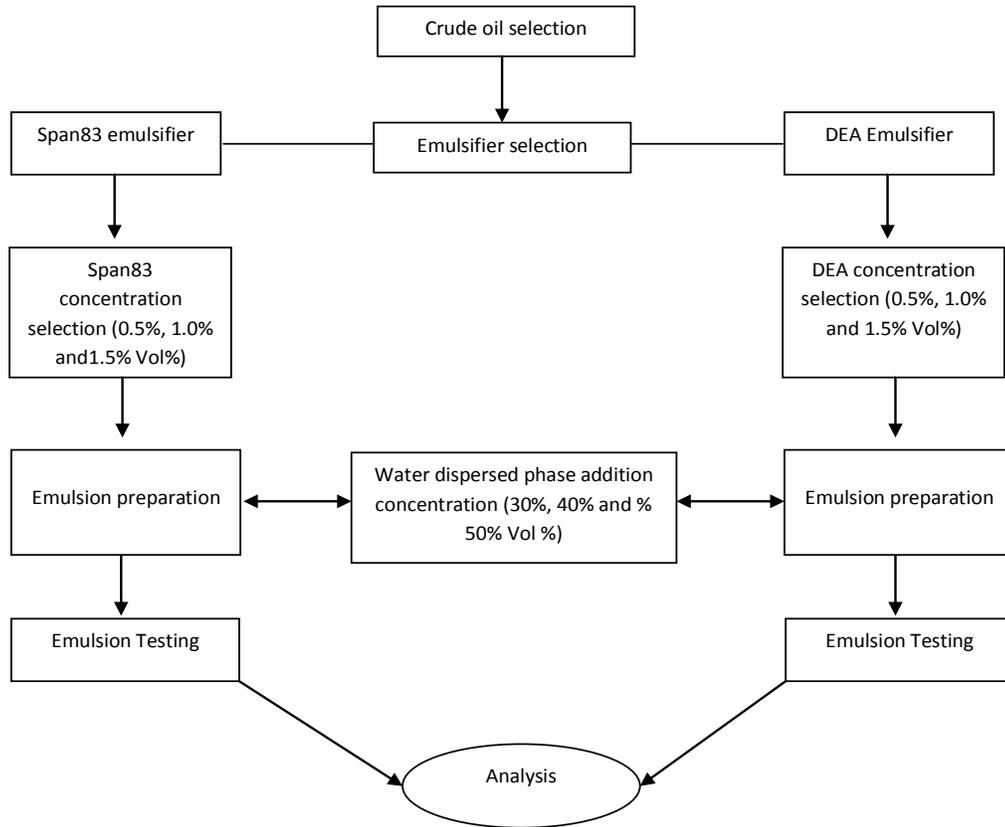


Figure 3. Flow diagram for the emulsion preparation procedures.

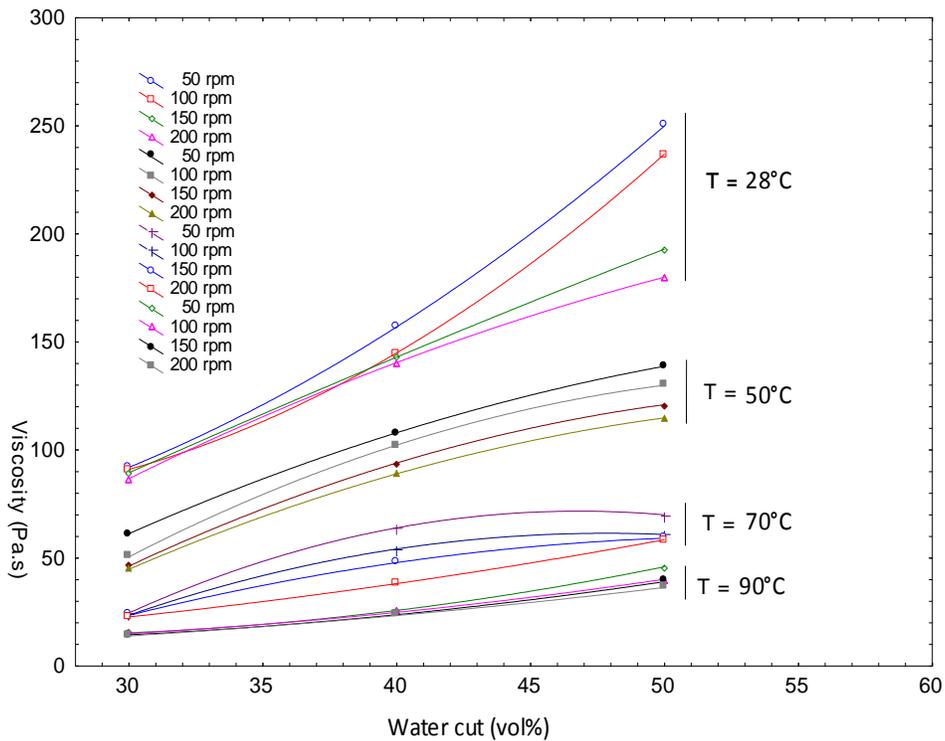


Figure 4. Effect of water content on the viscosities of the Span83 emulsions with addition concentration of 0.5% and at different temperatures and rotation speeds.

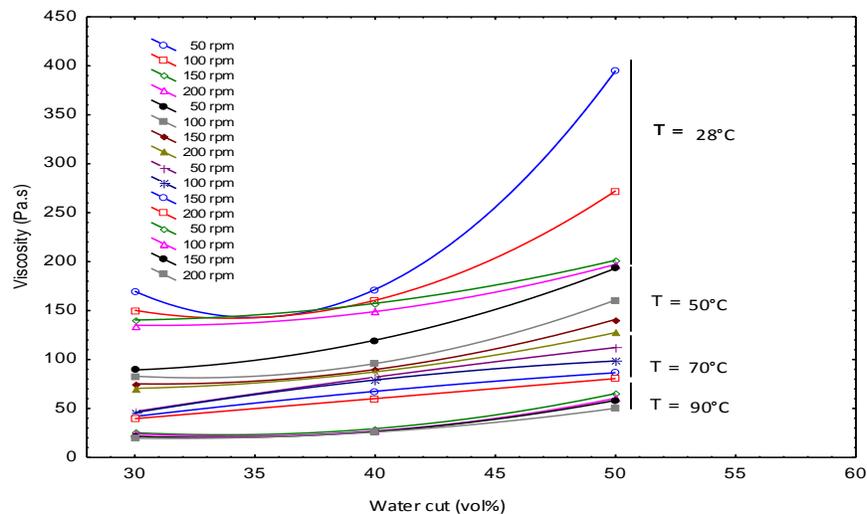


Figure 5. Effect of water content on the viscosities of the DEA emulsions with addition concentration of 0.5% and at different temperatures and rotation speeds.

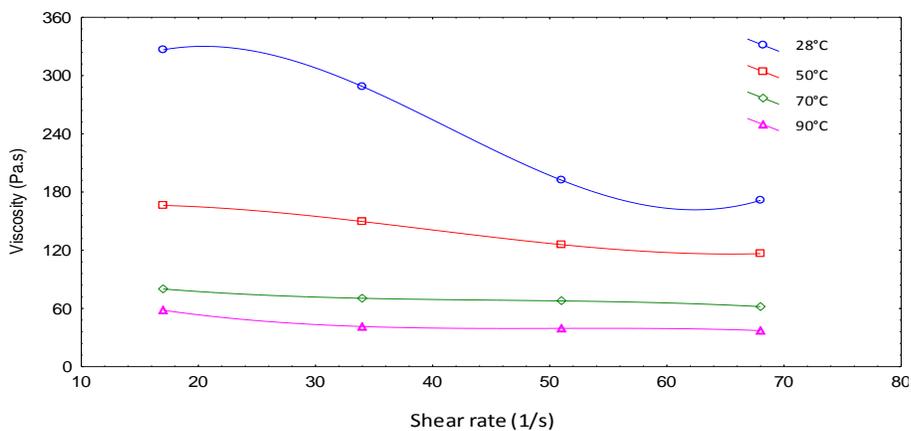


Figure 6. The shear rate dependence on viscosity of Span83 emulsion (1.0% emulsifier concentration and 50% water cut) with varied testing temperature.

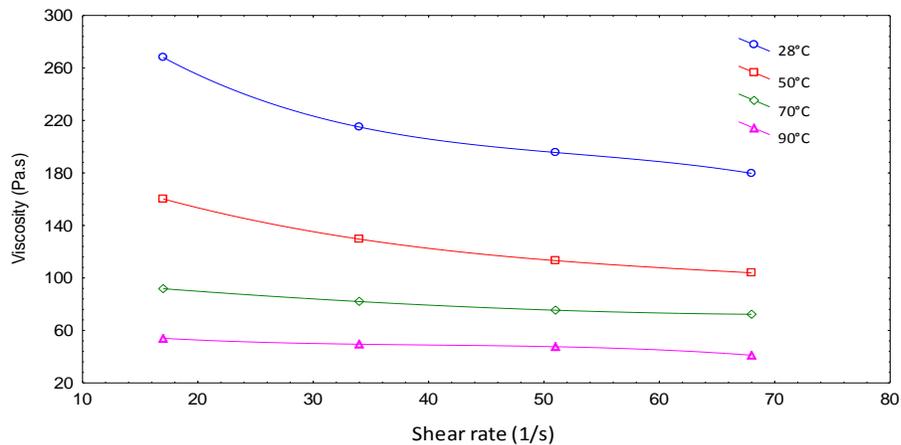


Figure 7. The shear rate dependence on viscosity of DEA emulsion (1.5% emulsifier concentration and 40% water cut) with varied testing temperature.

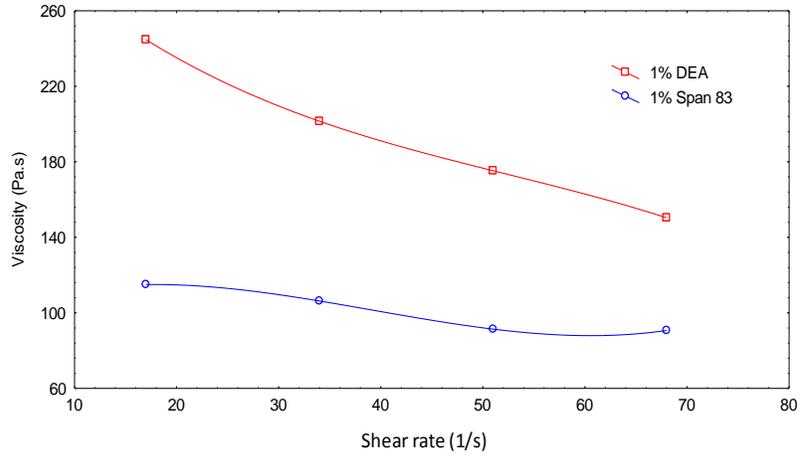


Figure 8. Effect of shear rate on the apparent viscosity of 1% DEA and Span83 emulsions at 28°C.

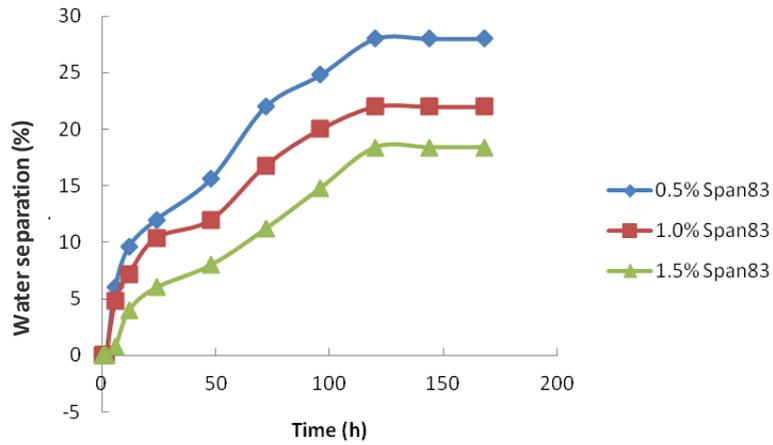


Figure 9. Water separation for Span83 (50% water content) emulsions at different concentrations.

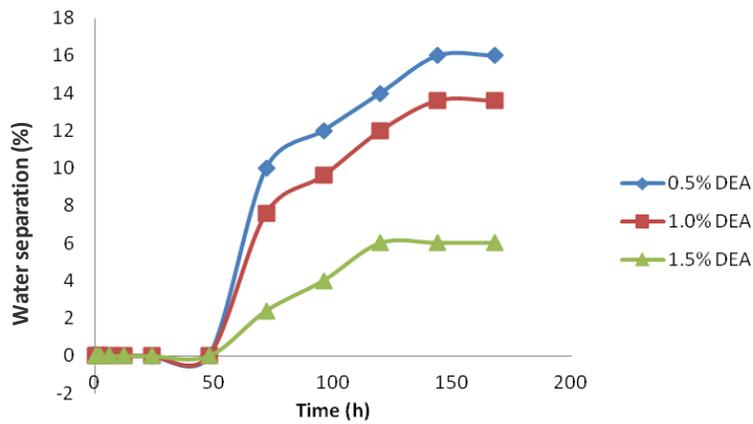


Figure 10. Water separation for Cocamide DEA (50% water content) emulsions at different concentrations.

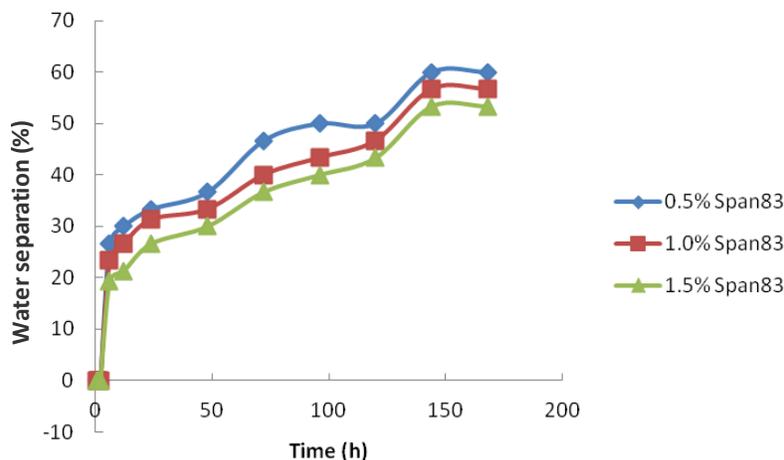


Figure 11. Water separation for Span83 (30% water content) emulsions at different concentrations.

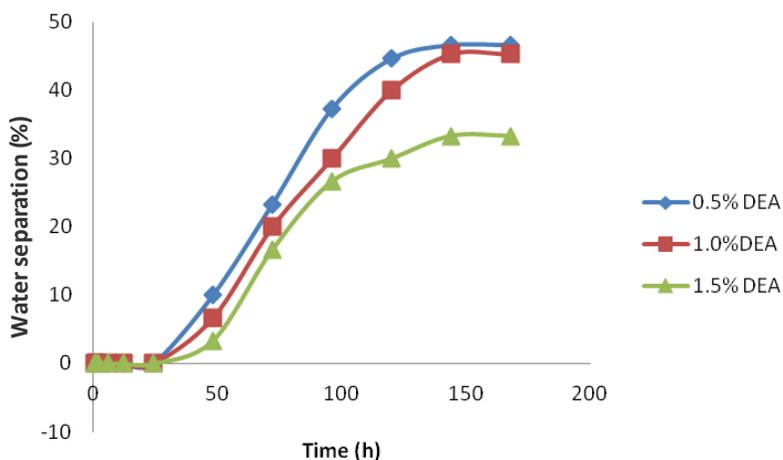


Figure 12. Water separation for Cocamide DEA (30% water content) emulsions at different concentrations.

percentage up to 28% at 0.5% addition concentration of Span83. The same behavior was observed for the DEA emulsifier as shown in Figure 10, where the water separation was reduced by increasing the surfactant concentration but with different percentages and behavior compared to the Span83 performance presented in Figure 9. The maximum separation percentage observed with the DEA emulsion was 16% at 0.5% addition concentration which is 43% less than that observed using Span83. Also, the water separation starts after 72 h which means that the DEA emulsion takes 12 times the time needed by the Span83 emulsion to start the separation. Increasing the emulsifier concentration means increasing the number of surfactant molecules involved and absorbed on the water-oil interface and that increases emulsion stability and reduces the water separation percentage. It is known that the DEA

molecules (M.Wt = 290) are shorter compared to the Span83 molecules (M.Wt = 1175) and that enables larger numbers of surfactant molecules to be absorbed on the water-oil interface which will lead to increase the interface tightness and reduce the water separation.

Figures 11 and 12 show the water separation tests results for the emulsions investigated using Span83 and DEA emulsifiers dissolved in 30% water content emulsion. Maximum water separation percentage up to 60% was observed when adding 0.5% Span83 and the water separation starts after 2 h. Surprisingly, maximum water separation percentage up to 47% was observed when using the DEA emulsifier at 0.5% addition concentration and the water separation started after 48 h. By comparing the maximum water separation percentages in Figures 11 and 12 for the 30% water content emulsions with those presented in Figures 9 and

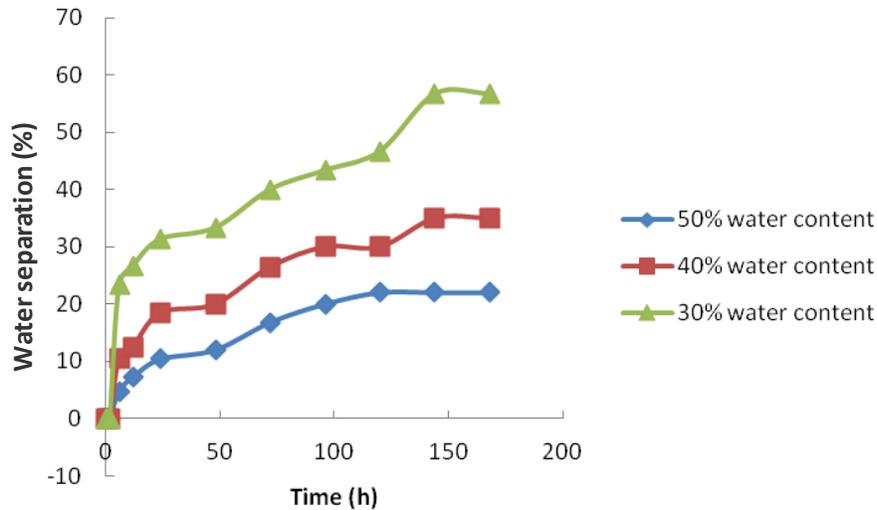


Figure 13. Effect of water content on the water separation for 1.0% Span83 emulsion.

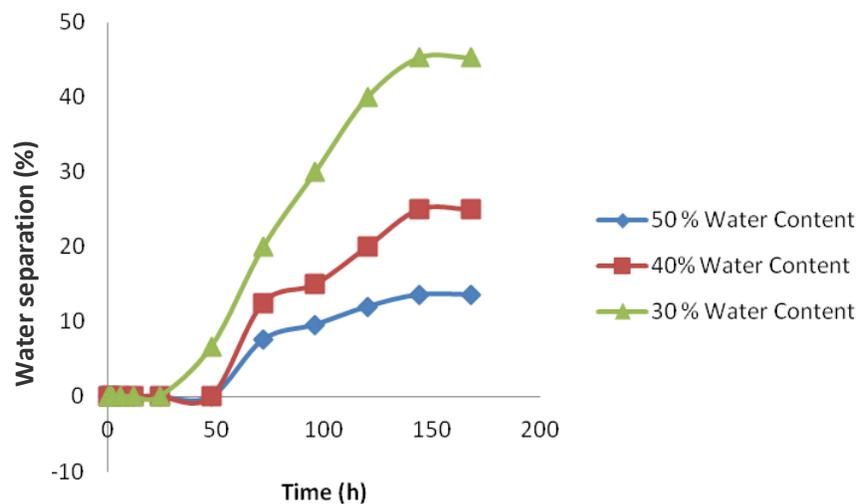


Figure 14. Effect of water content on the water separation for 1.0% DEA emulsion.

10 for the 50% water content emulsion, a clear conclusion pops up and highlights the effect of water content on the emulsifier performance in the emulsion formation process. It is believed that, increasing the water content (water droplets) will increase the emulsifiers molecules numbers involved in the emulsion formation process and converting the resulting emulsion towards being more non-Newtonian liquid (increasing the viscosity as discussed above) and that will result in more stable emulsion. This fact is presented graphically in Figures 13 and 14 that shows the effect of water content on the emulsion water separation using 1.0% Span83 and DEA, respectively. It is clear that the water separation reduces by increasing the water content from 30 to 50%. Such conclusion cannot be generalized, because the emulsion

stability depends on number of parameters acting in the same time with different effects.

Figures 15 and 16 compare the Span83 and DEA emulsions water separation percentages at the same operating conditions. Figure 15 compares the Span83 performance with the DEA by comparing the water separation percentage in 30% water content emulsion with 1.5% emulsifier concentration. It is clear that the DEA emulsion water separation starts after 48 h with maximum separation up to 34% while the Span83 emulsion water separation starts after 2 h with maximum water separation up to 54%. The same behavior was observed where a water separation comparison between Span83 and cocamide DEA (40% water content) emulsions at 1.5% concentrations was

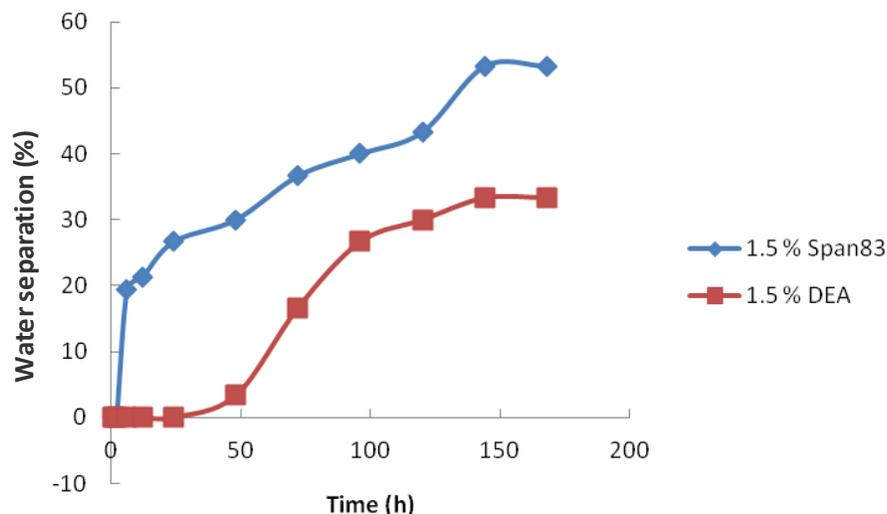


Figure 15. Water separation comparison between Span83 and Cocamide DEA (30% water content) emulsions at 1.5% concentrations.

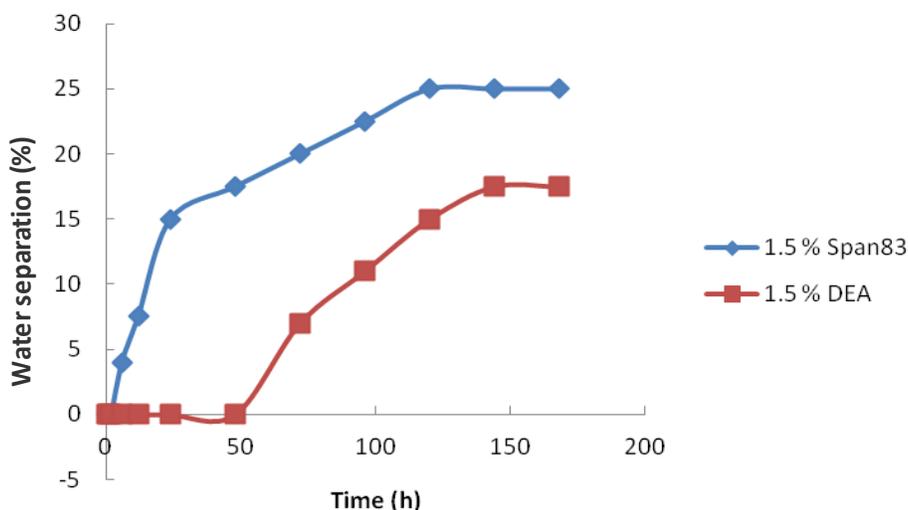


Figure 16. Water separation comparison between Span83 and Cocamide DEA (40% water content) emulsions at 1.5% concentrations.

held where the water separation starts after 2 h with maximum separation percentage up to 25% was observed when using Span83. The DEA emulsion needed 72 h to start separation with maximum separation percentage up to 17%. These figures support the fact that the smaller the emulsifier molecules, the higher the stability of the resulting emulsion.

Conclusions

The objective of this study is to investigate the effect of the environmentally friendly, nonionic emulsifying agent for crude oil emulsions (Cocamide DEA) in stabilization of

water-in-crude oil emulsions (W/O). Based on results of this study, it can be concluded that:

- i. The W/O emulsions show strong unstable behavior of water within the emulsion due to the absence of an emulsifying agent.
- ii. The stability of W/O emulsions enhances significantly by the addition of cocamide DEA.
- iii. The viscosity of W/O emulsions was found increases with water content and emulsifying concentration and decreases with rotational speed.
- iv. Stability of W/O emulsion enhances with cocamide DEA concentration.

v. High temperature reduces the W/O emulsion stability.

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