SUGAR-BASED ETHOXYLATED AMINE SURFACTANTS AS DEMULSIFIERS FOR CRUDE OIL EMULSIONS: 2- DEMULSIFICATION OF DIFFERENT TYPES OF CRUDES

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ABSTRACT

The present work studies demulsification of two types of crude oil emulsions by nine sugar-based ethoxylated amine surfactants. The effect of pH and salinity of aqueous phase of crude oil on emulsion stability was considered, and the correlation between demulsification rate and the type of crude was studied. Nine sugar-based ethoxylated amine surfactants were tested as demulsifiers for light and heavy crudes at different aqueous phase conditions. It was found that the light crude was more easily demulsified than the heavy crude. The experimental data showed that changes in pH or salinity of the aqueous phase of the emulsion enhance its stability and decrease the demulsification efficiency of the applied demulsifiers. Also, it has been shown that surfactants based on glucose octyl amine ethoxylates (GO) are the most effective in demulsifying the investigated emulsions. The data reveal that maximum demulsification efficiency is attained at a neutral pH whereas it decreases in both directions for either of the investigated crude oils. Furthermore, the results indicate that the percentage of water separation decreases as the salinity of the emulsion's aqueous phase increases. Light crudes showed better demulsification than heavy crudes under any test condition. The demulsification process for selected emulsions was monitored by optical microscopy.

KEYWORDS

demulsifiers; light crude; heavy crude; pH; salinity

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1. INTRODUCTION

Crude oil emulsions are of water-in-oil type. These emulsions are very hard to handle because they are stabilized by various naturally occurring surface active agents such as resins and asphaltenes (McLean et al., 1998; Sjöblom, 1992; Speight, 1999). Formation water with crude oil is in the centre of several problems, including: expenses for pumping or transporting water via pipeline or tankers, the corrosion of pipe work, pumps, production equipment and downstream overhead distillation columns, and the poisoning of downstream refinery catalysts (Speight, 1990; Speight, 1999; Vasquez and Mansoori, 2000). Thus, there are a number of commercial and operating reasons for removing the emulsified water from the crude oil. Consequently, the factors which either enhance or reduce oil emulsion stability are of considerable importance to the oil industry.

The methods currently available for demulsification can be broadly classified as electrical (Abdulrahman et al., 2006; Eley et al., 1988; Mohammed et al., 1993), mechanical (Chang and Fogler, 1994; Goldzal and Bourrel, 2000) and chemical demulsification (Garti et al., 1981; Rowan, 1992; Sjöblom et al., 1990a,b). The most widely applied method of treating emulsions involves the use of chemical additives to enhance emulsion separation processes. These chemical additives are commonly known as demulsifiers. These chemicals not only remove water from the emulsions, but also help reducing operating costs, waste and disposal costs and emissions, besides increasing profits with material recovery and increasing plant efficiency. The rate of water separation and demulsification affected by the applied chemicals depend on many factors. These factors are related to both the demulsifier itself, e.g. chemical composition and concentration, and the crude oil emulsion, such as age of emulsion, composition, salinity and pH of the aqueous phase.

In previous articles, we have investigated the demulsification efficiency of different surfactants (Abdel-Raouf et al., 2010a; Abdel-Raouf et al., 2010b; Zaki et al., 1996a; Zaki et al., 1996b), focusing on destabilization conditions of different synthesized emulsions. All these studies have given us insight into the factors relating to stability of synthetic water-in-oil emulsions. In one recent

work (Abdel-Raouf et al., 2010a), we have reported on the synthesis of some sugar-based ethoxylated amine surfactants, and tested them as demulsifiers for synthetic emulsions. The aim of the present work is to evaluate these surfactants as demulsifiers for two types of water-in-crude oil emulsions, i.e. light and heavy crudes. Some factors affecting demulsification rates were studied.

2. MATERIALS AND METHODS

2.1 Materials

Fresh water used throughout the experiments was double distilled de-ionized water. HCl, NaOH and NaCl used to adjust the pH and salinity of aqueous phase are AR chemicals obtained from Sigma-Aldrich Co. Light and heavy crudes used in the present work were obtained from Petrobel oil company, Egypt. In this paper, they are referred to as crudes A (heavy) and B (light).

Table 1. Codes and properties of the investigated demulsifiers.

<i>Designation</i>	<i>Code</i>	<i>HLB</i>	<i>MW (g mol⁻¹)</i>
GO400	1	10.10	790
GO1000	2	14.30	1395
GO2000	3	16.71	2396.4
GDe400	4	9.74	822.2
GDe1000	5	14.08	1424.7
GDe2000	6	16.53	2421.9
GDo400	7	9.42	850.1
GDo1000	8	13.8	1449.7
GDo2000	9	16.3	2451.9

2.2 Synthesis and characterization of the applied demulsifiers

Several ethoxylated sugar-based amine surfactants have been synthesized in our previous work (Abdel-Raouf et al., 2010a). The prepared surfactants were characterized by IR and ¹H-NMR spectroscopy. The hydrophilic-lipophilic balance (HLB) of those compounds ranged from 9.42 to 16.71, according to Griffin's formula (Griffin, 1954), whereas their molecular weights (MW) as measured by gel permeation chromatography (GPC) ranged from 822.2 to 2451.9 g mol⁻¹. These data are listed in Table 1.

Table 2. Physical properties of crude oils used in the experiments.

Crude oil	A (Land Belayim)	B (Marine Belayim)
API gravity at 60 °F	19.4	28.6
Viscosity at 60 °F	726.8	624.7
Specific gravity at 60 °F	0.938	0.884
Density (g cm ⁻³)	0.869	0.702
Surface tension at 60 °F (mN m ⁻¹)	28.9	22.4
Interfacial tension at 60 °F (mN m ⁻¹)	26.4	20.9

Table 3. Chemical composition of crude oils.

Crude oil	% water	% C ₁₅₋	% C ₁₅₊	Composition of C ₁₅₊			
				paraffins	naphthenes	aromatics	asphaltenes
A (Land Belayim)	7	7	86	19	28	37	16
B (Marine Belayim)	15	17	68	38	34	19	9

Table 4. Experimental conditions of the investigated emulsions.

Emulsion	Conditions	
	pH	Salinity (Molar, NaCl)
A (1-9)	1, 3, 7, 9 and 11	0, 0.25, 0.75 and 1
B (1-9)		

2.3 Preparation of W/O emulsions

2.3.1 Separation of formation water

The physical properties and compositions of the light and heavy crudes used in this research are shown in Tables 2 and 3, respectively.

Before preparing the re-constituted emulsions, the formation water was separated as follows: about 100 mL of crude oil was poured in a 100-mL cone-shaped graduated tube. The tube was then placed in a centrifuge, model Schimadzu MPW-350, and the speed of rotation was set at 1800 rpm for about 3 min. The amount of separated water was monitored and determined. The centrifugation process was repeated until all formation water was separated.

2.3.2 Re-constitution of emulsions

The re-constituted emulsions were prepared as mentioned in our previous work (Abdel-Raouf et al., 2010a). The experimental conditions used in this investigation are summarized in Table 4. To test the effect of salinity, the pH of the emulsions prepared with the nine demulsifiers was neutral.

To test the effect of pH, fresh distilled water was used to prepare the investigated emulsions. The demulsifiers were dissolved in the desired amount of water (an amount equivalent to that originally present in the crude oil). They were added at the recommended optimum concentration (300 ppm with respect to total volume of the emulsion) to the emulsion in 100-mL graduated cone-shaped tubes stopped with Teflon lids. The emulsion-demulsifier mixture was stirred in a shaker at 500 rpm for 15 min, and then placed in a thermostated water bath adjusted at 30 °C to cancel the effect of temperature. The amount of separated water was detected and registered for each condition (pH, type of crude oil and degree of salinity) after 6 h. In all experiments, a blank was utilized to compare the results with the amount of water separated in the absence of demulsifier.

2.4 Monitoring Emulsion stability by optical microscope

The stability of crude oils A and B before and after the addition of demulsifier was monitored by an Olympus optical microscope. The images were snapped with a camera installed at the microscope at a magnification of 20 times.

3. RESULTS AND DISCUSSION

In our previous publication (**Abdel-Raouf et al., 2010a**), nine sugar-based ethoxylated amine surfactants were prepared. They were used to break synthetic water-in-benzene emulsions stabilized by asphaltenes. We concluded that the most effective demulsifiers were derivatives with the octylamine group. Some factors controlling demulsification efficiency of the prepared demulsifiers were studied. In the present work, the prepared compounds were tested as demulsifiers for light and heavy crude oils.

3.1 Mechanism of demulsification process

Co-produced water generates many operational and economic problems. It is necessary to separate the water completely from the crude oil before transportation or refining. Demulsification of crude oil emulsion has attracted great attention by several authors (**González and Middea, 1991; Koots and Speight, 1975; Peramanu et al., 2001**), since these emulsions are highly stable by naturally occurring surface active components such as asphaltenes and resins. The role of asphaltenes and resins in stabilizing crude oil was extensively studied (**Cimino et al., 1995; Joshi et al., 2001; Leon et al., 2001; Sheu, 1996**). These components are arranged at the droplets interface and prevent them from approaching each other. The demulsification process starts when these components are replaced by other non-bulky components that allow the droplets to flocculate and decrease the interfacial elasticity of these droplets. Steps of emulsion breaking are illustrated in Figure 1. The oil film breaks when the film thickness reaches a critical level. The main role of the demulsifiers is either to replace part of

asphaltenes or combine with them. It is worthy to say that crude oil with lower asphaltene content will be subjected to demulsification processes more easily and faster.

3.2 Effect of crude oil emulsion on demulsification process

The experimental data showed that crude *B* was demulsified more easily than crude *A* by any of the applied demulsifiers. Figure 2 shows demulsification of crude oils *A* and *B* by the surfactants used (GOs) expressed as percentage of water separation (%), which was calculated with equation 1.

$$\% \text{ Water separation} = \frac{\text{Volume of separated water (mL)}}{\text{Total volume of water (mL)}} \times 100 \% \quad (1)$$

It is clear that crude *A* is more stabilized than crude *B* with asphaltenes and resins. It is also obvious that GO2000 gave maximum demulsification for the investigated crudes. In particular, the percentage of water separation after 6 hours for A3 and B3 was 95 % and 100 %, respectively. Our findings are in good agreement with those obtained by **Abdurahman and coworkers (2007)**.

3.3 Effect of the pH of the aqueous phase

The effect of pH of the emulsion's aqueous phase was studied at five different pH values, namely, 1, 3, 7, 9 and 11. All results are summarized in Table 5 for crude oil *A*, and Table 6 for crude oil *B*. We found that the maximum demulsification efficiency is attained at a neutral pH, from which it decreases in both directions. The effect of the pH of the aqueous phase on emulsion stability is illustrated in Figures 3 and 4 for crude

Figure 1. Steps of emulsion breaking.

oil A, and Figures 5 and 6 for crude oil B, in acidic and alkaline media. It is clear that the minimal percentage of water separation was obtained at very acidic or very alkaline medium. This runs in harmony with previous findings (Zaki et al., 1996b), and may be explained on the basis of the amphoteric nature of asphaltenes, which is highly affected by pH change. The water droplets will acquire a negative charge in basic medium and a positive charge in acidic medium due to the ionization equilibrium of asphaltenes. It is a well-known fact that electrical charges on the surface of dispersed water droplets cause electrostatic repulsion. Therefore, acidic or basic pH values result in enhanced emulsion stability by offering an electrostatic barrier to coalescence in addition to the already existing steric barrier.

3.4 Effect NaCl concentration of the aqueous phase

It is very important to consider the effect of salinity (NaCl concentration) on the demulsification ability of the investigated demulsifiers, since the actual oil-field emulsions are

Figure 2. Percentage of water separation as a function of time (1-6 h) for A1-A3 and B1-B3 emulsions at pH 7 without salt at 30 °C.

Figure 3. Percentage of water separation for A1-A3 at pH 1, 3 and 7.

Figure 4. Percentage of water separation for A1-A3 at pH 7, 9 and 11.

Figure 5. Percentage of water separation for B1-B3 at pH 1, 3 and 7.

Figure 6. Percentage of water separation for B1-B3 at pH 7, 9 and 11.

Figure 7. Percentage of water separation for A1-A3 at 0 M and 1 M salt concentrations.

often encountered with brine. The experimental results obtained for crudes A and B are listed in Tables 7 and 8 respectively. Figures 7 and 8 illustrate the dependence of the demulsification efficiency of the tested GO demulsifiers on the degree of salinity of the aqueous phase for crude oils A and B. Concentrations ranging between 0 and

1 M were used to represent the different salinities of the aqueous phase. It is obvious from the data of Figures 7 and 8 that the demulsification efficiency remarkably decreases by increasing the degree of salinity. This is attributed mainly to the decreased solubility of the demulsifiers in the aqueous phase as a result of increased salinity. Furthermore, it is clear that the most soluble demulsifier is still effective at high salt concentrations. It is only slightly affected by further increases in salt concentration, so it can be applied with high salinity levels. It is also obvious that destabilization of crude A was more hindered at high salinity than crude B. The present findings agree with those previously obtained by Zaki et al. (1996b).

3.5 Demulsification of synthetic emulsion compared to crude oils

The demulsification efficiency of the prepared demulsifiers was previously studied in water-in-benzene synthetic emulsions. In the present work, the prepared surfactants were evaluated as demulsifiers for two types of crude oils. Figure 9 shows the demulsification efficiency of the

Figure 8. Percentage of water separation for B1-B3 at 0 M and 1 M salt concentrations.

Figure 9. Demulsification efficiency of the investigated demulsifiers in synthetic emulsion and crude oils A and B: Demulsifier concentration = 300 ppm, fresh water and pH = 7, at 300 °C after 2 h.

Table 5. Percentage of water separation of A(1-9) emulsions at different pH values, at 30 °C, with fresh water.

Emulsion	pH 1																			
	1	2	3	4	5	6		1	2	3	4	5	6		1	2	3	4	5	6
A (Blank*)	---	---	---	---	---	3														
A1	---	---	10	17	22	30	A4	---	---	---	6	11	18	A7	---	---	---	---	5	11
A2	---	7	18	27	33	45	A5	---	---	3	9	19	24	A8	---	---	---	7	14	21
A3	5	13	21	30	39	50	A6	---	---	7	17	28	40	A9	---	---	4	10	19	28
	pH 3																			
	1	2	3	4	5	6		1	2	3	4	5	6		1	2	3	4	5	6
A (Blank*)	---	---	---	3	5	7														
A1	3	7	12	20	28	37	A4	---	---	4	10	21	33	A7	---	---	3	7	18	30
A2	9	18	29	38	50	62	A5	---	8	19	30	41	50	A8	---	5	12	20	28	40
A3	15	27	39	50	61	70	A6	3	12	21	32	50	64	A9	---	8	19	31	42	54
	pH 7																			
	1	2	3	4	5	6		1	2	3	4	5	6		1	2	3	4	5	6
A (Blank*)	---	---	3	6	8	9														
A1	44	50	58	65	73	82	A4	22	35	42	55	60	70	A7	15	22	30	37	44	50
A2	50	57	64	77	84	92	A5	32	42	47	58	69	84	A8	19	26	35	45	53	60
A3	54	59	67	79	87	95	A6	41	49	58	62	74	88	A9	24	30	39	48	60	72
	pH 9																			
	1	2	3	4	5	6		1	2	3	4	5	6		1	2	3	4	5	6
A (Blank*)	---	---	---	2	3	6														
A1	22	30	41	52	64	75	A4	18	30	40	52	63	72	A7	---	9	16	25	33	40
A2	33	45	53	61	72	80	A5	24	35	46	58	70	77	A8	7	19	27	36	47	53
A3	39	48	55	63	74	81	A6	30	41	50	61	79	80	A9	11	20	31	40	48	59
	pH 11																			
	1	2	3	4	5	6		1	2	3	4	5	6		1	2	3	4	5	6
A (Blank*)	---	---	---	---	---	2														
A1	---	5	9	18	29	40	A4	---	---	4	12	23	31	A7	---	---	5	12	21	29
A2	3	8	17	28	40	50	A5	---	6	11	20	29	37	A8	---	---	7	19	30	41
A3	9	19	30	41	53	65	A6	---	8	15	22	31	40	A9	7	15	24	33	42	57

(*) Blank refers to emulsion without demulsifiers

Figure 10. Maximum demulsification efficiency for the investigated demulsifiers.

examined here, and also to study the effect of asphaltene content on the demulsification process (Abdel-Raouf et al., 2010a). The data show that, under the same test conditions, the amount of water separated from the synthetic emulsion (stabilized by 0.25 % asphaltenes) was greater than the amount separated from the investigated crudes. It is also obvious that crude oil B (about 9 % asphaltenes) was demulsified more easily than crude oil A (about 16 % asphaltenes). This may be explained by the stabilizing effect of asphaltenes. However, when the experiment time was extended

Table 6. Percentage of water separation of B(1-9) emulsions at different pH values.

Emulsion	pH 1												pH 3											
	1	2	3	4	5	6	1	2	3	4	5	6	1	2	3	4	5	6	1	2	3	4	5	6
B (Blank*)	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
B1	3	11	20	33	42	54	B4	5	11	18	26	33	41	B7	8	12	16	24	33	40	48	51	58	63
B2	9	17	26	38	47	58	B5	14	19	25	33	40	49	B8	11	18	25	33	42	48	51	58	63	69
B3	14	22	30	41	53	63	B6	22	30	39	45	53	59	B9	17	27	35	41	47	51	58	63	69	77
pH 7																								
B (Blank*)	---	---	---	---	5	6	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
B1	19	29	40	50	62	71	B4	12	18	24	30	37	44	B7	14	19	26	33	40	49	58	63	69	77
B2	24	32	44	56	70	82	B5	19	28	35	40	49	57	B8	20	29	36	42	51	60	67	77	82	88
B3	28	35	48	58	69	80	B6	22	30	37	46	52	60	B9	26	33	40	48	54	61	67	77	82	88
pH 9																								
B (Blank*)	---	---	---	2	4	5	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
B1	33	43	51	59	70	80	B4	28	34	40	47	54	60	B7	12	16	24	29	33	40	49	58	63	69
B2	40	51	60	70	79	88	B5	33	39	48	57	63	70	B8	15	24	31	38	44	49	58	63	69	77
B3	48	55	62	74	86	92	B6	40	47	55	64	70	78	B9	23	31	36	44	52	60	67	77	82	88
pH 11																								
B (Blank*)	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
B1	20	26	35	41	50	59	B4	11	17	24	30	36	42	B7	7	12	20	25	31	36	44	49	58	63
B2	24	31	40	48	57	62	B5	15	22	30	38	44	50	B8	10	16	21	27	32	39	48	51	58	63
B3	30	38	46	57	67	78	B6	18	28	34	40	50	59	B9	13	18	24	32	40	44	49	58	63	69

(*) Blank refers to emulsion without demulsifiers

investigated demulsifiers in synthetic emulsions and crude oils A and B at the same test conditions, whereas Figure 10 shows the maximum demulsification efficiency for the prepared demulsifiers. Also, the demulsification efficiency of the prepared demulsifiers after two hours is tabulated in Table 9, whereas the maximum percentage of water separation is given in Table 10. The data for demulsification with synthetic emulsions are mentioned in order to compare the demulsification efficiency of the prepared demulsifiers with the light and heavy crudes

to 6 hours, the amount of water separated from crude B was very close – and sometimes exceeded – that of water separated from synthetic emulsion. For instance, the percentage of water separation from the synthetic emulsion was about 88 % by GDe1000 (demulsifier no. 5), whereas it was 93 % from crude B by the same demulsifier.

Table 7. Percentage of water separation of A(1-9) emulsions at different salt concentrations at 30 °C and pH 7.

Emulsion	0 M (Fresh water)																	
	1	2	3	4	5	6	1	2	3	4	5	6	1	2	3	4	5	6
A (Blank*)	---	---	3	6	8	9												
A1	40	44	53	68	73	80	A4	22	35	42	55	60	70	A7	15	22	30	37
A2	48	53	57	77	84	92	A5	32	42	47	58	69	84	A8	19	26	35	45
A3	54	59	64	79	87	95	A6	41	49	58	62	74	88	A9	24	30	39	48
	0.25M																	
	1	2	3	4	5	6	1	2	3	4	5	6	1	2	3	4	5	6
A (Blank*)	---	---	---	---	---	3												
A1	22	31	39	44	50	56	A4	18	25	33	40	47	52	A7	11	16	20	27
A2	27	33	41	50	57	64	A5	21	29	35	41	50	56	A8	14	19	26	31
A3	36	43	50	58	66	72	A6	25	31	39	44	52	60	A9	19	13	30	38
	0.75M																	
	1	2	3	4	5	6	1	2	3	4	5	6	1	2	3	4	5	6
A (Blank*)	---	---	---	---	---	---												
A1	12	15	19	23	29	33	A4	9	12	16	20	22	25	A7	5	8	10	13
A2	15	19	22	27	32	37	A5	10	14	17	21	25	28	A8	7	10	14	19
A3	17	21	24	29	33	39	A6	12	15	18	23	27	30	A9	8	12	15	20
	1M																	
	1	2	3	4	5	6	1	2	3	4	5	6	1	2	3	4	5	6
A (Blank*)	---	---	---	---	---	---												
A1	3	5	8	12	15	18	A4	---	---	3	7	10	14	A7	---	---	---	3
A2	7	11	18	25	30	38	A5	---	---	5	9	15	22	A8	---	---	4	8
A3	14	20	22	27	31	35	A6	---	4	8	11	16	23	A9	---	---	5	9

(*) Blank refers to emulsion without demulsifiers

Table 8. Percentage of water separation of B(1-9) emulsions at different salt concentrations at 30 °C and pH 7.

Emulsion	0 M (Fresh water)																	
	1	2	3	4	5	6	1	2	3	4	5	6	1	2	3	4	5	6
B (Blank*)	---	---	---	---	5	6												
B1	49	60	71	79	90	97	B4	32	47	52	61	74	80	B7	19	27	35	42
B2	53	59	69	83	90	100	B5	40	59	70	81	89	93	B8	24	33	40	49
B3	60	70	77	87	94	100	B6	52	65	71	84	90	97	B9	30	40	49	58
	0.25 M																	
	1	2	3	4	5	6	1	2	3	4	5	6	1	2	3	4	5	6
B (Blank*)	---	---	---	---	---	---												
B1	44	50	55	61	68	74	B4	29	35	40	46	50	55	B7	14	18	26	33
B2	48	53	59	64	70	77	B5	33	38	42	49	53	59	B8	16	22	27	35
B3	54	59	67	72	79	84	B6	38	44	47	52	58	64	B9	20	24	30	37
	0.75 M																	
	1	2	3	4	5	6	1	2	3	4	5	6	1	2	3	4	5	6
B (Blank*)	---	---	---	---	---	---												
B1	40	43	48	53	60	66	B4	25	29	33	39	42	46	B7	11	14	19	22
B2	44	49	54	60	65	72	B5	29	35	40	43	49	51	B8	12	16	20	24
B3	50	56	62	67	73	80	B6	31	37	42	49	52	57	B9	14	18	27	30
	1 M																	
	1	2	3	4	5	6	1	2	3	4	5	6	1	2	3	4	5	6
B (Blank*)	---	---	---	---	---	---												
B1	22	27	33	38	42	50	B4	15	19	22	26	31	37	B7	8	11	15	18
B2	26	30	37	44	52	60	B5	17	21	28	31	36	40	B8	10	14	17	20
B3	30	33	40	48	56	66	B6	20	25	29	32	37	42	B9	12	17	21	25

(*) Blank refers to emulsion without demulsifiers

3.6 Monitoring demulsification process by optical microscopy

It was previously mentioned that optical microscopy can be used in the characterization of crude oil emulsions (Manar et al., 2010; Yunus et al., 2010). In this respect, crude oils A and B without demulsifiers and then with 300 ppm of GO2000 (code No. 3) were examined by optical

microscopy. The images are shown in Figure 11. It is clear that the water droplets are very small, and remain away from each other in the absence of demulsifier. On the other hand, when the demulsifier is added, it combines with some asphaltene molecules, causing the dispersed water droplets to approach each other and accumulate as larger ones. At the end, repeated coalescence and flocculation lead to phase separation.

Figure 11. Demulsification process for crude oils A and B: (i) crude oil A without demulsifier; (ii) crude oil A with 300 ppm GO2000 after 6 h; (iii) crude oil B without demulsifier; (iv) crude oil B with 300 ppm GO2000 after 6 h.

Table 9. Demulsification efficiency of the investigated demulsifiers in synthetic emulsions and crude oils A and B (Demulsifier concentration: 300 ppm; fresh water, pH 7 at 30 °C after 2 h).

Designation	Code	Synthetic emulsion	Crude oil A	Crude oil B
GO400	1	87	44	60
GO1000	2	100	53	59
GO2000	3	100	59	70
GDe400	4	85	35	47
GDe1000	5	88	42	59
GDe2000	6	90	49	65
GDo400	7	60	22	27
GDo1000	8	62	26	33
GDo2000	9	66	30	40

Table 10. Maximum demulsification efficiency of the investigated demulsifiers after test time (Demulsifier concentration: 300 ppm; fresh water, pH 7 at 30 °C).

Designation	Code	Maximum Water separation (Synthetic emulsion)	Test Time (hour)	Maximum Water separation (Crude A)	Time (hour)	Maximum Water separation (Crude B)	Test Time (hour)
GO400	1	87	2	80	6	97	6
GO1000	2	100	2	92	6	100	6
GO2000	3	100	2	95	6	100	6
GDe400	4	85	2	70	6	80	6
GDe1000	5	88	2	84	6	93	6
GDe2000	6	90	2	88	6	97	6
GDo400	7	60	2	50	6	60	6
GDo1000	8	62	2	60	6	67	6
GDo2000	9	66	2	72	6	80	6

4. CONCLUSIONS

Nine sugar-based ethoxylated amine surfactants were tested as demulsifiers for light and heavy crudes at different aqueous phase conditions. It was found that the light crude was more easily demulsified than the heavy crude. The experimental data showed that changes in pH or salinity of the aqueous phase of the emulsion enhance its stability and decrease the demulsification efficiency of the applied demulsifiers.

5. REFERENCES

- Abdel-Raouf, M. E.-S.; Abdul-Raheim, A.-R. M.; Abdel-Azim, A.-A. A. Surface Properties and Thermodynamic Parameters of Some Sugar-Based Ethoxylated Amine Surfactants: 1 – Synthesis, Characterization, and Demulsification Efficiency, published online in **Journal of Surfactants and Detergents**, May 7th, 2010a, available at www.springerlink.com/content/1097-3958.
- Abdel-Raouf, M. E.-S.; Abdul-Raheim, A.-R. M.; Maysour, N. E.-S.; Mohamed, H. Synthesis, Surface-Active Properties and Emulsification Efficiency of Trimeric-Type Nonionic Surfactants Derived from Tris(2-aminoethyl)amine, published online in **Journal of Surfactants and Detergents**, August 4th, 2010b, available at www.springerlink.com/content/1097-3958.
- Abdurahman, H. N.; Yunus, R. M.; Jemaat, Z. Study on demulsification of water-in-oil emulsions via microwave heating technology. **Journal of Applied Sciences**, v.6, p. 2060-2066, 2006. [doi:10.3923/jas.2006.2060.2066](https://doi.org/10.3923/jas.2006.2060.2066)
- Abdurahman, H. N.; Yunus, R. M.; Jemaat, Z. Chemical demulsification of water-in-crude oil emulsions. **Journal of Applied Sciences**, v.7, p. 196-201, 2007. [doi:10.3923/jas.2007.196.201](https://doi.org/10.3923/jas.2007.196.201)
- Chang, C.-L.; Fogler, H. S. Stabilization of Asphaltenes in Aliphatic Solvents using Alkyl benzene-derived Amphiphiles. 1. Effect of the Chemical Structure of Amphiphiles on the Asphaltenes Stabilization. **Langmuir**, v.10, p. 1749-1757, 1994. [doi:10.1021/la00018a022](https://doi.org/10.1021/la00018a022)
- Cimino, R. S.; Correra, A. D.; Lockheart, T.P.
- Solubility and phase behavior of asphaltenes in hydrocarbon media**, In: Sheu, E.Y.; Mullins, O. C. (Eds.), **Asphaltenes: Fundamentals and Applications**. New York: Plenum Press, 1995, p. 7-130.
- Eley, D. D.; Hey, M. J.; Symonds, J. D. Emulsions of Water in Asphaltene-Containing Oils. 1. Droplet Size Distribution and Emulsification Rates. **Colloids and Surfaces**, v.32, p. 87-101, 1988. [doi:10.1016/0166-6622\(88\)80006-4](https://doi.org/10.1016/0166-6622(88)80006-4)
- Garti, N.; Aserin, A.; Zaidman, B. Polyglycerol esters: optimization and techno-economic evaluation. **J. Am. Oil Chem. Soc.**, v 58, p. 878-883, 1981. [doi:10.1007/BF02672963](https://doi.org/10.1007/BF02672963)
- Goldzal, A.; Bourrel, M. Demulsification of crude oil emulsions: Correlation to microemulsion phase behavior. **Ind. Eng. Chem. Res.**, v.39 (8), p. 2746-2751, 2000. [doi:10.1021/ie990922e](https://doi.org/10.1021/ie990922e)
- González, G.; Middea, A. Peptization of asphaltene by various oil soluble amphiphiles. **Colloids and Surfaces**, v.52, p. 207-217, 1991. [doi:10.1016/0166-6622\(91\)80015-G](https://doi.org/10.1016/0166-6622(91)80015-G)
- Griffin, W. C. Calculation of HLB values of non-ionic surfactants, **J. Soc. Cosmet. Chem.**, v.5, p. 249-256, 1954.
- Joshi, N. B.; Mullins, O. C.; McFadden, J. Asphaltene Precipitation from Live Crude Oils. **Energy & Fuels**, v.15, p. 979-986, 2001. [doi:10.1021/ef010047l](https://doi.org/10.1021/ef010047l)
- Koots, J. A.; Speight, J. G. Relation of petroleum resins to asphaltenes. **Fuel**, v.54, p. 179-184, 1975. [doi:10.1016/0016-2361\(75\)90007-1](https://doi.org/10.1016/0016-2361(75)90007-1)
- Léon, O.; Contreras, E.; Rogel, E.; Dambakli, G.; Espidel, J.; Acevedo, S. The Influence of the Adsorption of Amphiphiles and Resins in Controlling Asphaltene Flocculation. **Fuel**, v.15, p. 1028-1032, 2001. [doi:10.1021/ef010032n](https://doi.org/10.1021/ef010032n)
- McLean, J. D.; Spiecker, P. M.; Sullivan, A. P.; Kilpatrick, P. K. **The Role of Petroleum Asphaltenes in the Stabilization of Water-in-Oil Emulsions**, In: Mullins and Sheu (eds.), **Structure and Dynamics of Asphaltenes**. New York: Plenum Press. p. 377-422, 1998.
- Mohammed, R. A.; Bailey, A. I.; Luckham, P. F.; Taylor, S. E. Dewatering of crude oil emulsions 2.

Interfacial properties of the asphaltic constituents of crude oil. **Colloids Surfaces A: Physicochem. Eng. Aspects**, v.80, p. 237-242, 1993. [doi:10.1016/0927-7757\(93\)80203-Q](https://doi.org/10.1016/0927-7757(93)80203-Q)

Peramanu, S.; Singh, C.; Agrawala, M.; Yarranton, H. W. Investigation on the Reversibility of Asphaltene Precipitation. **Energy & Fuels**, v.15, p. 910-917, 2001. [doi:10.1021/ef010002k](https://doi.org/10.1021/ef010002k)

Rowan, B. **The use of chemicals in oilfield demulsification**, Industrial Applications of surfactants III. Cambridge: Royal Society of Chemistry, 1992.

Sheu, E. Y.; Physics of asphaltene micelles and microemulsions: theory and experiment. **J. Phys. Condens. Matter**, v. 8, p. 125-141, 1996. [doi:10.1088/0953-8984/8/25A/009](https://doi.org/10.1088/0953-8984/8/25A/009)

Sjöblom, J. Stabilization and Destabilization of Water-in-Crude Oil Emulsions from the Norwegian Continental Shelf. Correlation with Model Systems. **Advances in Colloid and Interface Science**, v.41, p. 241-271, 1992. [doi:10.1016/0001-8686\(92\)80014-O](https://doi.org/10.1016/0001-8686(92)80014-O)

Sjöblom, J.; Söderlund, H.; Lindblad, H. S.; Johansen, E. J.; Skjærvø, I. M. Water-in-crude oil emulsions from the Norwegian continental shelf. Part II, Chemical destabilization and interfacial tensions. **Colloid & Polymer Science**, v.268, p. 389-398, 1990a.

Sjöblom, J.; Urdahl, O.; Høiland, H.; Christy, A. A.; Johansen, E. J. Water-in-crude oil emulsions Formation, characterization, and destabilization. **Progress in Colloid & Polymer Science**, v.82, p.

131-139, 1990b. [doi:10.1007/BFb0118251](https://doi.org/10.1007/BFb0118251)

Speight, J. G. **Fuel Science and Technology Handbook**, New York: Marcel Dekker, p. 61-65, 1990.

Speight, J. G. **The chemistry and technology of petroleum**, New York.: Marcel Dekker, p. 22-30, 1999.

Vasquez, D.; Mansoori, G. A. Identification and measurement of petroleum precipitates, **Journal of Petroleum Science and Engineering**, v. 26, p. 49-55, 2000. [doi:10.1016/S0920-4105\(00\)00020-6](https://doi.org/10.1016/S0920-4105(00)00020-6)

Yunus, R. M.; Abdulrahman, H. N.; Isaaka, S. A. Decolorization and Characterization of petroleum emulsions. **Journal of Applied Sciences**, v.10, p. 215-220, 2010. [doi:10.3923/jas.2010.215.220](https://doi.org/10.3923/jas.2010.215.220)

Zaki, N. N.; Abdel-Raouf, M. E.-S.; Abdel-Azim, A.-A. A. Propylene Oxide-Ethylene Oxide Block Copolymers as Demulsifiers for Water-in-Oil Emulsions, I. Effect of Molecular Weight and Hydrophilic-Lipophilic Balance on the Demulsification Efficiency. **Monatshefte für Chemie**, v.127, p. 621- 629, 1996a.

Zaki, N. N.; Abdel-Raouf, M. E.-S.; Abdel-Azim, A.-A. A. Propylene Oxide-Ethylene Oxide Block Copolymers as Demulsifiers for Water-in-Oil Emulsions, Effects of Temperature, Salinity, pH-Value, and Solvents on the Demulsification Efficiency. **Monatshefte für Chemie**, v.127, p. 1239-1245, 1996b.