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ORIGINAL RESEARCH PAPER

STUDY REGARDING THE DESTABILIZATION OF STABLE EMULSIONS FROM SUPLAC AREA

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Abstract: Emulsions from the wells in the Suplac area create great difficulties in removing water due to their specifications. A complex study was conducted in order to eliminate water from emulsions using alkaline-surfactants. The choice of surfactant was made after the chromatographic SARA analysis of emulsions and the determination of their physical properties: density, viscosity, organic acidity. The samples were taken from two wells in the Suplac area. In the case of samples from A well the variation of density is 907 - 955 kg·m^{-3} for crude oil and 928 - 970 kg·m^{-3} for emulsion, while the rheological behavior of the emulsion varies between 0.680 to 0.995 Pa·s at a temperature of 25 °C and between 0.049 to 0.328 Pa·s at a temperature of 80 °C. For samples from B well the variation of density is 855 - 905 kg·m^{-3} for crude oil and 939 - 970 kg·m^{-3} for emulsion, while the rheological behavior of the emulsion varies between 0.149 to 0.797 Pa·s at a temperature of 25 °C and between 0.014 to 0.397 Pa·s at a temperature of 80 °C. The justification for choosing R - DP surfactant like reagent was based on laboratory tests which showed a maximum efficiency at 80 °C (95.69 for B and 98.75 % for A).

Keywords: *aromatic, asphaltene, emulsion breaking agents, resin, saturated, water/oil emulsion*

INTRODUCTION

Removing water from oil-water mixtures can still be quite difficult due to the high stability of the emulsions they form. Problems raised by this process appear in both oil exploitation and wastewater treatment with a high content of oil products [1 – 3]. The stability of formed emulsions requires finding solutions either classical, based on the mass transfer phenomena and chemical reactions [4, 5], or based on unconventional methods such as nanotechnologies applied to wastewater with a high content of oil products [6 – 9]. The most important fact is that the amount of generated waste does not increase after the procedure is applied [10].

As a result of oil exploitation, in bore holes water-oil emulsion may appear. According to the literature, emulsions can be classified in three categories according to the predominant water droplet dimensions: finely dispersed emulsions [11 – 14] (water droplets size below 20 µm), medium dispersed emulsion (water droplets size between 20 - 50 µm) and high dispersed emulsion (water droplets size is higher than 50 µm). Currently, the most applied methods for water removing from crude oil are: electrical emulsion breaking and chemical emulsion breaking. The efficiency of electrical emulsion breaking is high, but this methods disadvantage of using is represented by its relatively high costs.

A frequently used method is the chemical emulsion breaking [15]. Chemical agents used in this method neutralize the emulsifier layer formed on the surface of the particles, resulting in phase separation. The commonly used emulsion breaking agents are: nonionic (poliethoxylate alkyl phenols, ethoxylate fatty acids), cationic (organic amines or quaternary salts of amines) or anionic (alkyl aryl sulphonates) [16 – 19]. Their choice depends on the type of crude oil and residual water composition, on the rock type, temperature, etc.

An efficient surfactant meets the following requirements:

- decreases the interfacial tension of the water/oil system;
- minimum loss in the deposit;
- similar mobility to that of the fluids with which it comes into contact;
- stability, from a chemical point of view, in formation waters;
- solubility or dispersability in water or crude oil.

The asphaltene content in the crude oil makes possible their classification according to the colloidal instability index (IIS) value [16] (Table 1).

Table 1*. Asphaltene stability or instability depending on the values of the colloidal instability index (IIS)*

IIS	Asphaltene stability
< 0.7	Stable asphaltenes
0.7 - 0.9	Moderate instability
> 0.9	Unstable asphaltenes

This paper presents the analysis of the efficiency of emulsion breaking agents on the destabilization of emulsions formed in samples from Suplac area, in order to increase the inflow of fluids formation.

MATERIALS AND METHODS

This study had two lines of work: determining the proprieties of oil samples collected from two wells in the Suplac area, Romania; and testing of surfactants to destabilize the formed emulsion. The two sample sets are noted in the present study with A and B.
For this purpose a total of five samples have been taken from the two wells. Samples from the two wells were listed according to Table 2.

Table 2. *Liste of samples from the two wells*

Well	Sample No.	Well	Sample No.
A	1	B	6
	2		7
	3		8
	4		9
	5		10

The physical-chemical properties of the crude oil samples determined in the laboratory were: the type of crude oil, water content, viscosity, content of saturated compounds (SAT), asphaltene (ASF), resin (RES), aromatic (ARM), (SARA), organic acidity.
The stability of emulsion was tested using a Turbiscan device and a Zetasizer device [4]. Determination of the colloidal instability index was realized using the following equation [20, 21]:

$$IIS = \frac{SAT + ASF}{ARM + RES} \tag{1}$$

where: IIS represents the colloidal instability index;
SAT represents saturated compounds content, mass [%];
ASF represents asphaltene content, mass [%];
ARM represents aromatic content, mass [%];
RES represents resin content, mass [%].
The emulsion breaking process was carried out in the laboratory at three different temperatures in a thermostat pressurized reactor. The amount of the test sample was of 100 mL. Working temperatures were 25, 50 and 80 °C. A number of three demulsifiers was tested. They are part of the latest generation of surface-active substances. The amount of emulsion breaker added was 50 mL. Their characteristics are shown in Table 3.

Table 3. *Characteristics of the surfactants tested for the elimination of water from the emulsions*

Surfactant	**Ionic charge**	**Compositions**
E - 96B	nonionic	polioxipropilen-polioxietilen copolymers
R	cationic	cationactive substances (incompatible with active anion substances)
R-DP	cationic	cationactive substances (compatible with anionic surfactant substances)

In order to calculate the efficiency of tested surfactants the amount of water separated by the centrifugation method for each sample was taken into consideration [20].

RESULTS AND DISCUSIONS

The results *via* SARA method for crude oil samples are presented in Table 4.

***Table 4.** The saturate, aromatic, resin and asphaltene content of oil crude samples*

Sample No.	Well	Saturate (SAT) mass [%]	Aromatic (ARM) mass [%]	Resin (RES) mass [%]	Asphaltene (ASF) mass [%]	IIS	RES/ ASF	RES+ ASF
1	A	40.33	31.06	21.77	6.84	0.89	3.18	28.61
2		39.29	31.25	22.44	7.02	0.86	3.19	29.46
3		40.44	29.56	22.89	7.11	0.90	3.21	30
4		39.96	31.22	21.84	6.98	0.88	3.12	28.82
5		39.95	31.72	21.57	6.76	0.87	3.19	28.33
6	B	52.23	29.59	14.28	3.9	1.27	3.66	18.18
7		50.65	30.66	14.88	3.81	1.19	3.90	18.69
8		50.56	30.88	15.12	3.44	1.17	4.39	18.56
9		49.87	31.69	14.45	3.99	1.16	3.62	18.44
10		49.88	31.98	14.66	3.48	1.14	4.21	18.14

The two types of crude oils are distinguishable as follows: the samples of crude oil from well A have a variable resin content with values between 21.77 and 22.89 % (mass), compared to 14.28 and 15.12 % (mass) for the samples of crude oil originating from well B. The resin/asphaltene ratio varies between 3.18 and 3.21 % (mass) for well A, and between 3.62 to 4.39 % (mass) for well B, while the total concentration of resins and asphaltenes is greater in the case of well A (between 28.33 and 30 % (mass)) compared to well B (18.14 to 18.69 % (mass)).

Therefore the colloidal instability index calculated with equation 1 was smaller for the crude oil originating from well A (0.86 - 0.90), than the one of the crude oil originating from well B (1.16 - 1.27).

High IIS values were found for the samples from both well A and well B proving that water removal at high temperatures can create problems in terms of organic deposits. Thus, further testing of Zeta potential and appropriate surfactant choice was necessary in order to destabilize the emulsion.

The choice of surfactants for breaking the emulsions should be done depending on the organic acidity and viscosity at different temperatures. Besides these two properties we also needed to determine the density of the samples taken from the two wells.

The crude oil originating from well A has an organic acidity of 4.3 mg $KOH \cdot g^{-1}$ sample, on the other hand the crude oil from well B had an organic acidity medium value of 2.1 mg $KOH \cdot g^{-1}$ sample.

The presence of organic acidity and of high amounts of polar compounds in the samples, lead us to choose alkaline surfactants.

Figure 1 presents the density variations with the temperature.

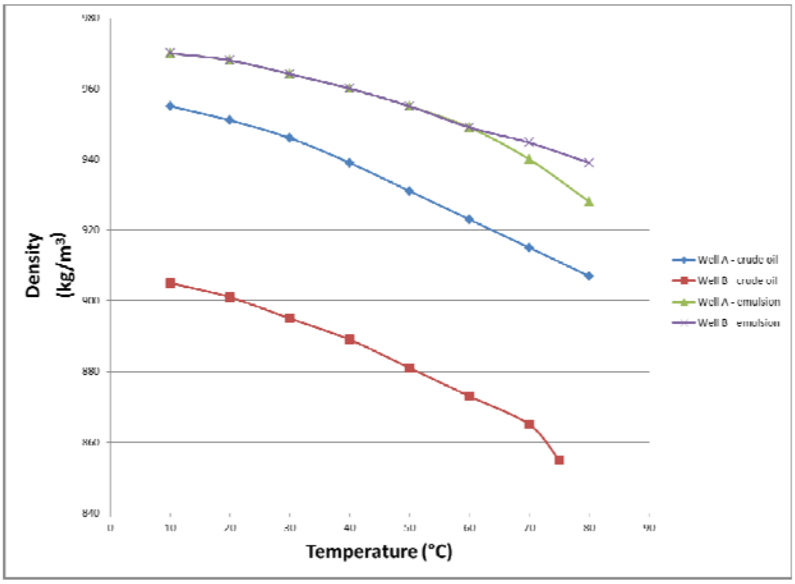

Figure 1. *The fluid density vatiation with the temperature*

The high densities of the emulsions collected from well B at temperatures superior to 50 °C, show that the emulsions are more stable. In this case additional information is required and, also, it is necessary to follow the rheological behavior of the emulsions.

The rheological behavior of the crude oil and emulsions was analyzed via the viscosity calculation at the following temperatures: 25, 50 and 80 °C; the results obtained being listed in Figures 2 and 3.

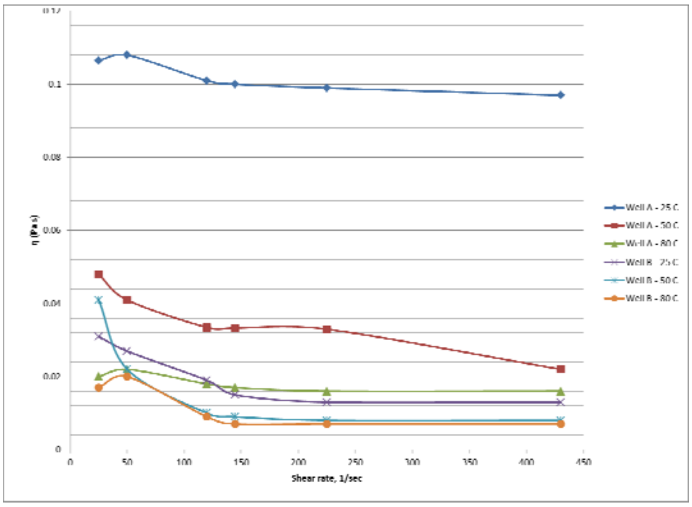

Figure 2*. Rheological behavior of crude oils for A and B wells*

Figure 3 shows that for all the tested working temperatures the viscosity of the emulsion originating from well A are higher than those of the emulsion originating from well B.

The high viscosity values based on the shear stress indicate a greater stability of emulsions collected from well A than of the ones collected from well B.

Thus, the coalescence phenomenon is slow and the emulsion stability from well A is greater. In this case, the treatment process with dispersing agents will also be more difficult to realize.

The samples stability determined with TURBISCAN (26 - 28 °C) was similar.

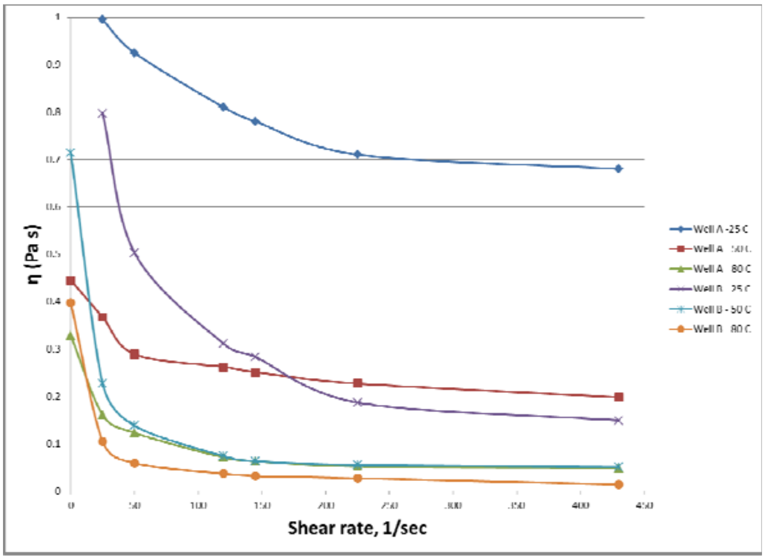

Figure 3. *Rheological behavior of emulsion for A and B wells*

Therefore, in the present study we present a single chart that describes a straight line (Figure 4), which means that water-oil emulsion is very stable [16].

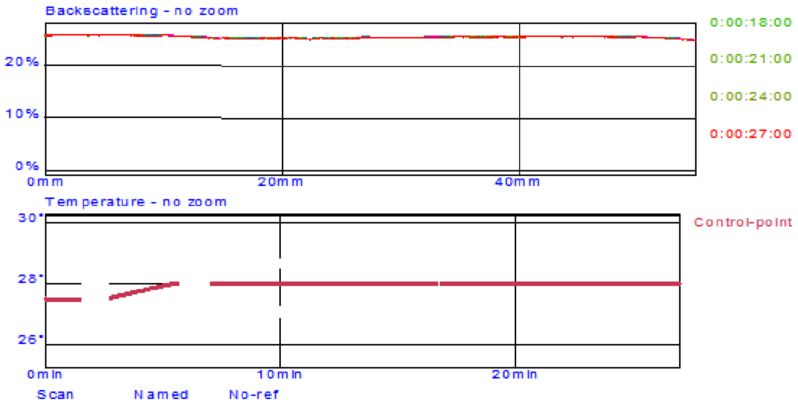

Figure 4. *The stability of emulsion determined on TURBISCAN*

Thus, removing water from this emulsion will be very difficult and possible only under special working conditions; namely at high temperatures and with the help of very strong emulsion breakers.

The TURBISCAN device could not determine the stability of the samples from the two wells, at a temperature higher than 30 °C. In that case, the Zeta potential was determined. Under normal circumstances it is considered that the zeta potential for emulsion with a high stability is between -30 mV and -51 mV. The Zeta potential measured for the samples from the two wells at 50 to 80 °C are shown in Table 5.

Table 5. *The Zeta potential measured for the samples from the two wells at 50 to 80 °C*

Temperature, [°C]	Sample	Zeta potential, [mV]
50	A	-30
	B	-38
80	A	-51
	B	-51

Analyzing the values shown in Table 5 we can observe that the Zeta potential values are between -30 mV and -38 mV at temperatures of 50 °C, indicating a greater stability at this temperature. At 80 °C the emulsions have the Zeta potential value of approximately -51 mV for both sets of samples. Correlating all the results presented above we recommended that the emulsions destabilization be done at 80 °C. However, since the emulsions original from the Suplac area could present anomalies in the stability behavior we also tested them at 25 and 50 °C.

The samples from A and B wells were tested with the proposed surfactants. The surfactant concentration was 1 %, thus respecting the conditions imposed in operation requiring a maximum concentration of 1 % for emulsion breakers. The water volumes separated by centrifugation depending on temperature and on the emulsion breaker agent are presented in Tables 6, 7 and 8.

***Table 6**. Emulsion breaking tests for samples from A and B wells at 25 °C*

Sample		**Emulsion Breaker Agent**	**Separated water volume [mL]**	
Well A	**Well B**		**Well A**	**Well B**
1	6	E- 96	46	40
		R	35	33
		R-DP	49	48
2	7	E- 96	44	40
		R	31	32
		R-DP	47	49
3	8	E- 96	41	49
		R	32	36
		R-DP	47	54
4	9	E- 96	46	41
		R	33	39
		R-DP	49	52
5	10	E- 96	40	35
		R	35	27
		R-DP	44	46

***Table 7**. Emulsion breaking tests for samples from A and B wells at 50 °C*

Sample		**Emulsion Breaker Agent**	**Separated water volume [mL]**	
Well A	**Well B**		**Well A**	**Well B**
1	6	E- 96	46	48
		R	35	33
		R-DP	62	59
2	7	E- 96	44	40
		R	31	32
		R-DP	55	51
3	8	E- 96	41	49
		R	32	36
		R-DP	59	54
4	9	E- 96	48	41
		R	33	39
		R-DP	57	52
5	10	E- 96	40	45
		R	35	37
		R-DP	51	54

***Table 8**. Emulsion breaking tests for samples from A and B wells at 80 °C*

Sample		Emulsion Breaker Agent	Separated water volume [mL]	
Well A	**Well B**		**Well A**	**Well B**
1	6	E- 96	60	68
		R	58	73
		R-DP	72	89
2	7	E- 96	56	70
		R	51	62
		R-DP	78	81
3	8	E- 96	61	79
		R	52	66
		R-DP	76	84
4	9	E- 96	58	71
		R	53	69
		R-DP	74	82
5	10	E- 96	60	65
		R	55	67
		R-DP	79	76

The volume of water separated by centrifugation from samples taken from well A varies between 31 mL to 49 mL at 25 °C, it goes up to 62 mL at 50 °C and reaches the maximum values at 80 °C, up to 79 mL.

For the samples from well B the water volume separated by centrifugation varies between 32 mL to 54 mL at 25 °C, it goes up to 59 mL at 50 °C and reaches the maximum values at 80 °C, up to 89 mL,.

The volume of water separated by centrifugation has the highest values in case of tests with performed with the R-DP surfactant. The efficiency of emulsion breaking for the R-DP surfactant are shown in Figures 6 and 7.

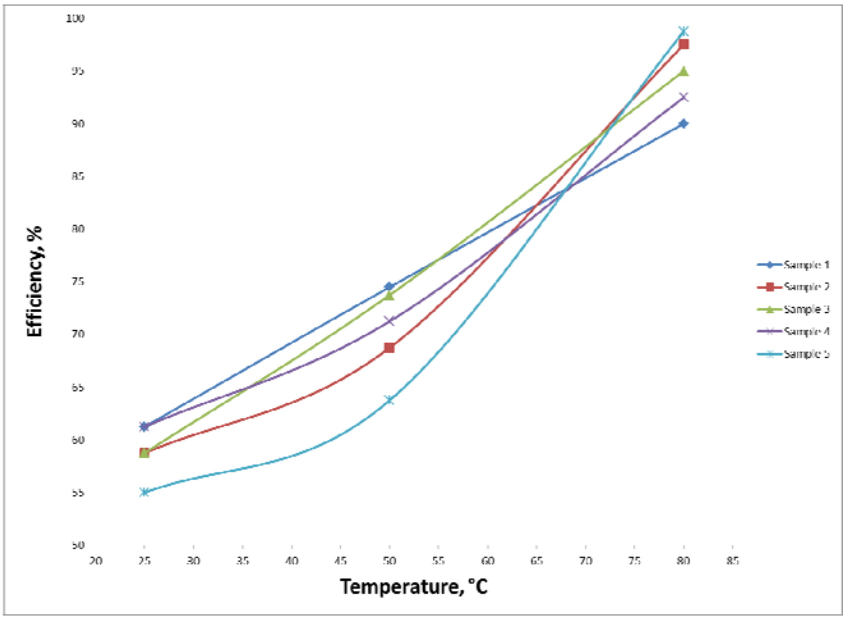

***Figure 6.** The efficiency of emulsion breaking for the R-DP surfactant for well A samples*

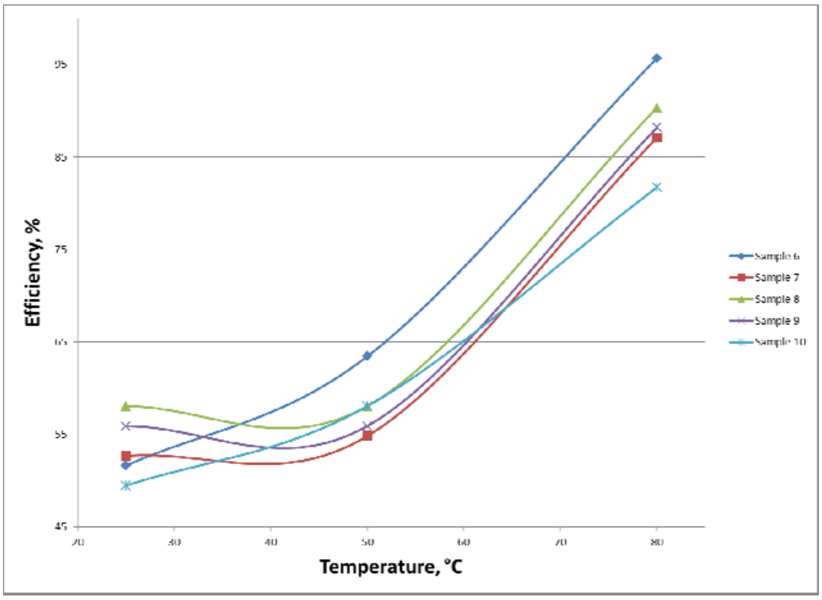

Figure 7. *The efficiency of emulsion breaking for the R-DP surfactant for B well samples*

CONCLUSIONS

The present study brings into question the directions of research for discovering the necessary measures needed in order to eliminate water from water/oil emulsions. The need to study this topic arose from the difficulties encountered in removing water from oilfield deposits. The resources available in the fields of Suplac area have a high content of asphaltenes, therefore the values of IIS are between 0.87 and 1.29.

In order to make the correct choice of surfactants required for the destabilization of emulsions, we created an experimental program which initially began with the stability analysis of emulsions starting by determining their initial composition. Based on the data obtained by SARA chromatographic analysis, organic acidity, density and viscosity, we determined that the formed samples for sample A are more stable than those for sample B. The verification of these conclusions was made by determining the Zeta potential that ranged between -30 mV and -38 mV at 50 °C and -51 mV at 80 °C.

The tests carried out on the selected surfactants at different temperatures (25, 50 and 80 °C) highlighted that R-DP surfactant presented the highest efficiency, as follows: 61.25 % at 25 °C, 77.5 % at 50 °C and 98.75 % at 80 °C for samples taken from well A, and a maximum efficiency of 61.25 % at 25 °C, 63.44 % at 50 °C and 95.69 % at 80 °C for samples from well B.

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