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Application of Imidazolium based ionic liquid Nano-emulsions for the removal of H_2S from crude oil

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Abstract

Hydrogen sulfide is one of the most dangerous contaminants in crude oil and natural gas that have to be removed prior to the transfer and refining. In this study, hydrophobic ionic liquid, i.e. 1-ethyl-3-methylimidazolium methylflour, [EMIM] [NTf2], was used as scavenger for the reduction of the H_2S. Due to its ionic nature, [EMIM] [NTf2] forms nanoemulsion in crude oil media and hence can dissolve H_2S polar molecules within its core. Determination of H_2S was carried out using well-known UOP-163 potentiometric titration. The effect of [EMIM] [NTf2] on the H_2S concentration was investigated via two methods: dynamic and static. Dynamic method performed to check the effect of required dosage for the removal of H_2S and also investigate effect of contact time. In the static methods a number of tests were designed with central composite design (CCD) to investigate the effect of three factors, i.e. scavenger dosage, reaction time and temperature, as well as the interaction between them on the concentration of H_2S via response surface methodology (RSM). Among these three factors and according to the F value, scavenger dosage and time had the great influence on the response, respectively. In comparison, temperature had very low effect on the response. The resulted model was also statistically significant with non-important LOF index.

Keywords: Nano-emulsion, Design of Experiments, H_2S, Optimization, Scavenger, Ionic Liquids

1. Introduction

Usually the amount of sulfur in the crude oil that has been discovered between 0.05 to 5% by weight has been reported. Crude oil contains some sulfur compounds, namely H_2S which has a large number of environmental hazards and sever corrosion effects in the oil industry. As a result, environmental regulations reduced the legal standard amount of H_2S in oil and gas to be transported, exported or refined. There are several methods to reduce the concentration of H_2S. Scavenger technology is one of the most

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common methods especially in low concentrations of H_2S (500 ppmw >). Among the chemical scavengers, those that have fast reaction time, low HSE effects and low equivalent reaction ratio are the best choices. Ionic liquids are a new class of chemical compounds with outstanding properties and features such as non-flammable, Thermal stability, high electrical conductivity, low vapor pressure, high polarity, common organic solvent for extraction and high density. These compounds have a large/small organic cations and organic or inorganic anion, low melting point and are mainly in liquid state. The most important feature of these compounds is the possibility of modification and tuning of their physical properties by changing the type of anion and cation. Ionic liquids are primarily based cationic imidazolium , pyridinum , perilydinum and phosphoniom with different chaines and anions such as tetraflourborate and hexaflourphosphate.

2. Experimental

Recognized international standards ASTM, UOP, API, IP, DIN and ISO standard methods to identify and measure sulfur compounds in oil and oil products have provided. One of the finest and most widely used methods is UOP 163 standard method based on potentiometric titration which was used for the measurement of H_2S in crude oil in this project. But the rest of the sulfur-containing compounds must have to be measured using chromatography. However, in this study the operational methods of the static method (under a constant concentration of scavenger) and dynamic (with variable concentration of scavenger) used both methods are described below.

3. Results and discussion

3.1 Dynamic method

According to the evaluation method based on measuring and tracking changes in crude oil potential while gradually increasing over a period of time is scavenger. This method is usually at intervals of one minute about 10 μl Scavenger a certain amount of crude oil (5 gr about) is added and the potential changes with time as shown in Figure 6 is recorded.
Preliminary analysis indicates that the electrode potential of H_2S in crude oil has been lowered as long as scavenger added to the crude oil. Depending on the concentration of H_2S electrode potential changes within a specific area is between -700 to -1000 mV. Therefore, this measure can monitor the amount of H_2S in crude oil. Experiments showed that when crude oil is free of H_2S (< 1 ppm) electrode potential shift to higher than -700 mV.

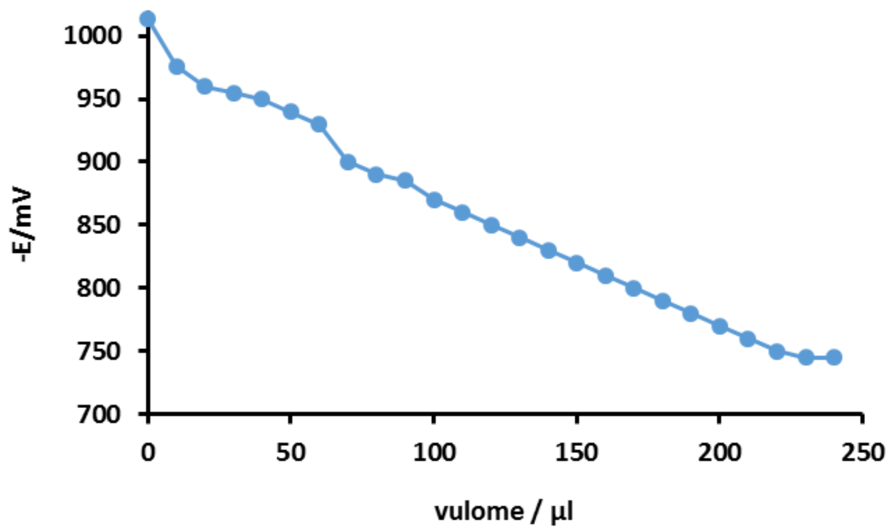

Figure 1. Change of potential with increasing of scavenger in 10 microliter intervals and 1 minute reaction time for each addition.

3.2 Static method

In this method, the amount of hydrogen sulfide in crude oil measured using UOP163, and for more detailed study of the absorption of H_2S and evaluation of effective parameters and their interaction with response surface methodology was used to determine the effect of different factors. Three parameters that are expected to be a factor affecting absorption of H_2S include scavenger dosage in the range of 2-10 , temperature from 25 to 50 °C and time from 15 to 45 minutes . For this purpose a series of experiments designed with CCD. The potential of crude oil was selected as a response in this project. The level of each of the factors is given in Table 1. These levels are based on previous experience worked in the laboratory.

Table 1 The level of each of the factors discussed in the absorption of H_2S.

Factor	[scavenger] / [H_2S] (A)	Temperature ^0C (B)	TIME min (C)
High level	5	50	**45**
Low level	2	25	**15**

Accordingly, using Design Expert7.1.3 software 18 tests were designed (given in Table 2). The result of each run was inserted into the software and data analysis was started. This design consists of 4 replicates.

Table 2 Matrix tests and Response.

STD	Run	[S]/[H_2S]	Temp	Time	Response (-mV)
5	1	2	25	45	**945**
13	2	6	37.5	15	**956**
3	3	2	50	15	**954**
11	4	6	25	30	**960**
4	5	10	50	15	**928**
1	6	2	25	15	**970**
6	7	10	25	45	**712**
16	8	6	37.5	30	**900**
12	9	6	50	30	**836**
17	10	6	37.5	30	**923**
18	11	6	37.5	30	**923**
2	12	10	25	15	**872**
10	13	10	37.5	45	**923**
14	14	6	37.5	45	**849**
15	15	6	37.5	30	**900**
7	16	2	50	45	**899**
8	17	10	50	45	**832**
9	18	2	37.5	30	**959**

Table 2 is based on tests done and the results are entered in the last column for the response. These values are also entered in the software after the calculation, the results are given below. These results fitted with different models and suitability of different types of models is presented in Table 3.

Table 3 Comparison of models to fit the data

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	Remark
Mean vs Total	1.493E+007	1	1.493E+007			
Linear vs Mean	29494.90	3	9831.63	22.87	< 0.0001	
2FI vs Linear	3734.50	3	1244.83	6.00	0.0112	Suggested
Quadratic vs 2FI	364.11	3	121.37	0.51	0.6889	
Cubic vs Quadratic	1388.60	4	347.15	2.62	0.1868	Aliased

The model with the highest degree and the most capable of the relationship between the independent variables, F (factors) and outcome (response) is selected. According to this strategy, 2FI (two factor interaction) model was selected for the explanation and fitting of the experimental data. In addition, the model with a non-important LOF is a good model and a model which is aliased is the worst have be omitted. The F-value of each term in the model is greater than the critical F value. LOF of possible models are compared in Table 4. As once can see, the quadratic model has non-important LOF means the ability of model to fit the experimental data.

Table 4 Comparison of LOF to all models.

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	Remark
Linear	5488.377778	11	498.9434343	2.829546887	0.2123	
2FI	1753.877778	8	219.2347222	1.243297101	0.4742	Suggested
Quadratic	1389.766667	5	277.9533333	1.576294896	0.3758	
Cubic	1.166666667	1	1.166666667	0.006616257	0.9403	Aliased
Pure Error	529	3	176.3333333			

The ANOVA table was also given in table 5. According to the F value, time, scavenger dosage and temperature affect the response, respectively. The interaction of the BC was not important and so omitted and the data was refitted again. The obtained results are given in table 5.

Table 5 ANOVA table of the fitting of experimental data.

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	Remark
Model	33157.4	5	6631.48	33.7927347	< 0.0001	significant
A-[S][H2S]	13690	1	13690	69.76158234	< 0.0001	significant
B-TEMP	360	1	360	1.834490113	0.2006	significant
C-TIME	15444.9	1	15444.9	78.70421206	< 0.0001	significant
AB	2738	1	2738	13.95231647	0.0028	significant
AC	924.5	1	924.5	4.711072526	0.0507	significant
Residual	2354.877778	12	196.2398148			
LOF	1825.877778	9	202.8753086	1.150521599	0.5080	not significant

According to this selected method, the change of potential with time, temperature and scavenger dosage in Figures 2, 3 and 4 are shown

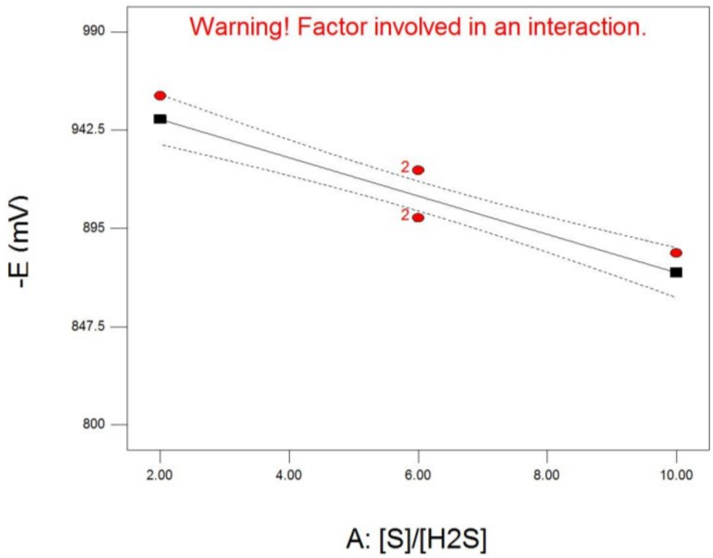

Figure 2 Change of potential with Scavenger

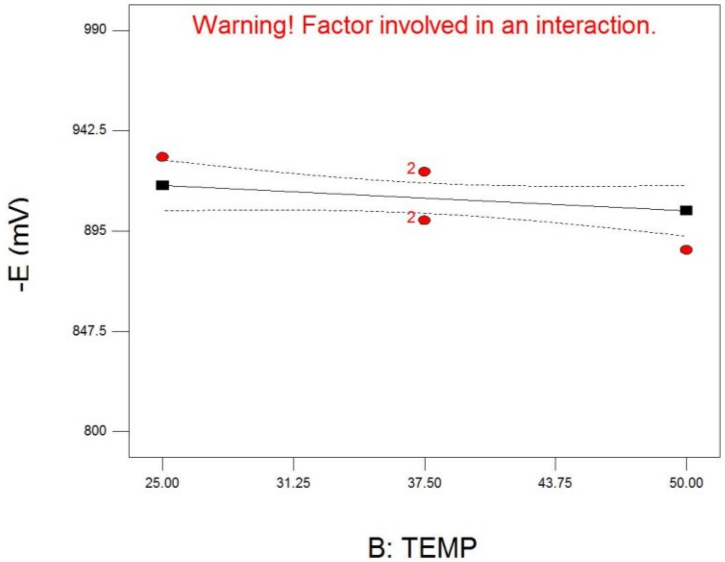

Figure 3 Changes of potential versus temperature

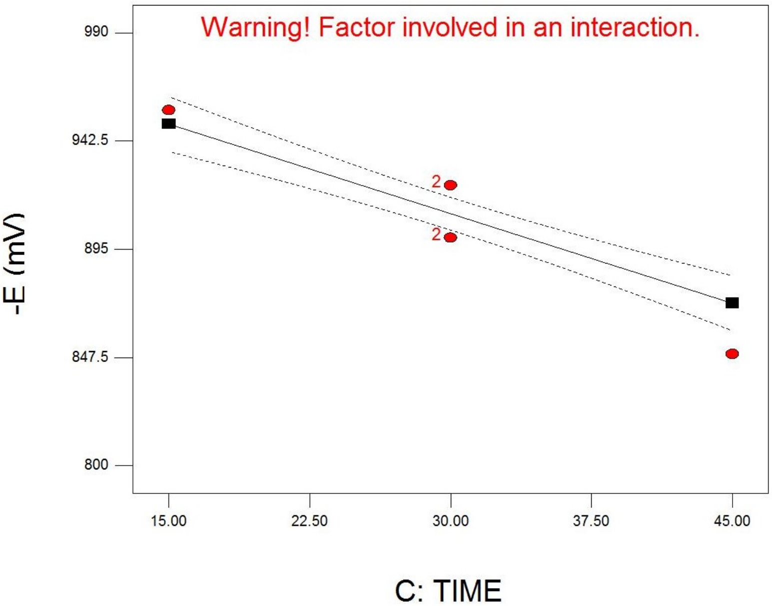

Figure 4 Change of potential with time

According to the results of tests designed, all three factors are considered to be important, the temperature, time and the scavenger dosage because their F-value is larger than critical F value. Figure 5 illustrates the interaction of Time and scavenger dosage via a two dimensional garph. The obtained equation according to the actual values is given below:

(Equation 1)

$$R1 = (+1113.71111) - (17.75000 \times [s][H2S]) - (2.70000 \times TEMP) - (1.54500 \times TIME) + (0.37000 \times [s][H2S] \times TEMP) - (0.17917 \times [s][H2S] \times TIME)$$

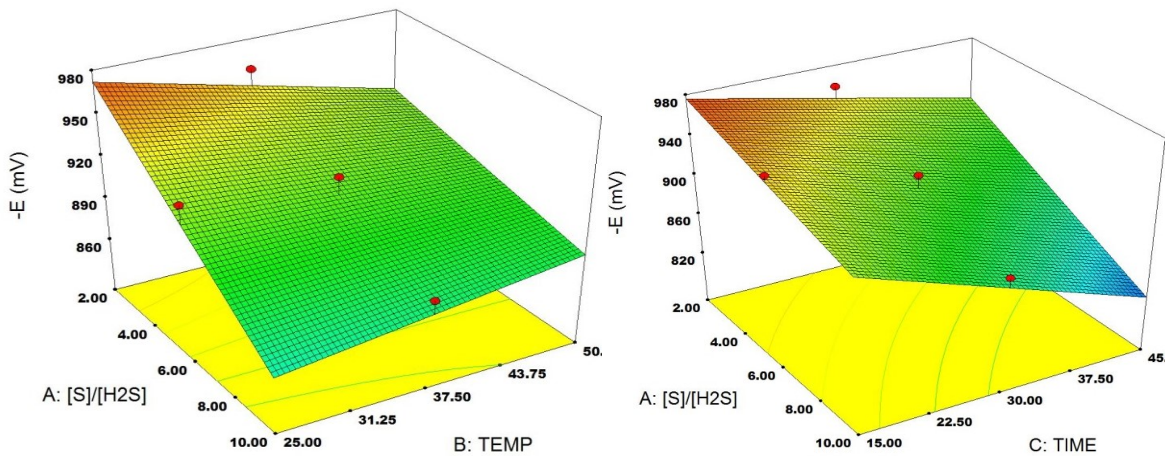

Figure 5. Interaction of scavenger dosage with temperature (Left) and time with scavenger dosage (Right)

The above graph shows that the temperature and scavenger dosage have greater interaction than time with scavenger dosage and can influence the response importantly. Effect of scavenger dosage is more important at lower temperature but the effect of temperature is reversed at a specific scavenger dosage. This behavior did not seen in the interaction of time with scavenger dosage.

4. Conclusion

Scavenger performance is very dependent on the operating conditions, in particular the time, temperature, mixing speed and the type of crude oil. Among them, crude oil type is the most important with great and non-expectable impact on the H_2S. In some cases, positive and some cases negative! The results show that the choice of this type of ionic liquid to remove H_2S is good; even though better ones can be use. The ionic liquid creates a nanoemulsion in the nonpolar medium and so can dissolve polar compounds of crude oil, namely H_2S. The experiment design parameters such as temperature, time and the scavenger dosage were displayed that all three parameters are effective on the removal of H_2S.

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