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RESEARCH PAPER

Optimization Technique for the Evaluation of Physiochemical Properties of Cationic Surfactant in Presence of Alkali / Metal Halide Salt and their Effects on Acidic Crude Oil

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Abstract

Despite the considerable progress in the safe and effective use of renewable energy, oil is still the world's first choice as an energy source. Meanwhile, after the traditional oil recovery methods, a large quantity of crude oil remains deposited in the oil well. The chemical enhances oil recovery method implies the injection of surfactants to increase oil recovery. The basic principle of surfactant flooding is to decrease the imbalance tension force to increase the mobility ratio of oil. In this study, extensive lab work has been done to identify the synergic effect of surfactant, alkali, and salt on acidic crude oil. The design expert generated the composition of the injection fluid, and the obtained results in terms of viscosity, surface tension, pH, and conductivity are reported in this paper. Also, the optimum point or the concentration combination of surfactant, alkali, and salt generated by the design expert has the maximum effect on the acidic crude oil. A remarkable decline was noticed in the acidic crude and surface tension's viscosity at an optimum point. In contrast, an increase in pH and conductivity of acidic oil was observed. The results reported herein correspond to a significant understanding of the interaction of surfactant-alkali and salt solution with acidic crude and change in the crude oil properties.

Keywords:
Acidic Crude Oil,
Alkali,
Mobility,
Optimization,
Surface Response,
Surface Tension

Introduction

Currently, crude oil has been one of the principal energy sources, and it is significantly achieving the need for future energy demand [1]. Therefore, to meet the demand, it is required to expand the production level in the next few years, which can be attained by unearthing the new oil fields or enhancing production from the present oil fields. Initially, oil is produced by using the pressure of the reservoir itself. Up to one-third of the crude remains left in the reservoirs after secondary enhance oil recovery in most of the cases [1-5]. Although the enhanced oil recovery technique is needed to upgrade the depletion of oil [6]. A wide range of injection materials such as surfactants, polymer, nanomaterials, and alkali are generally utilizing to improve the

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displacement and sweep efficiency [7-14]. The polymers such as polyacrylamide are generally used to improve the viscosity of the injecting fluid to enhance the mobility ratio [15-17]. Surfactants are also used to influence the trapped oil movement by emulsification, changing the rock wettability and interfacial rheological properties [18-20]. The suitable surfactants for any reservoir are chosen after some evaluation steps such as reservoir temperature and salinity, pH, the chemical structure of surfactant, rock permeability and adsorption of surfactant, etc.

The various experimental results covering the surfactant flooding aspects are available in the literature [21-23]. Olajire discussed in detail the ASP flooding in his review, including the displacement and interaction, future possibility, and the challenges of the ASP flooding [24]. Sheng study reviewed the surfactant-based enhance oil recovery technology and summarizes the various simulation as well as the experimental work in carbonate and shale reservoirs [25]. Chemical Surfactant-based enhance oil recovery technique is a complex technique, and a good understanding is needed to understand how any surfactant interacts in difficult reservoir operating conditions. The injection of surfactant with alkali can decrease the surfactant adsorption, increase ionic resistance, and reduce the interfacial tension [26]. The alkali reacts with the organic acid components in acidic crude oils, forming surfactants by the in-situ saponification process [27-28]. Besides generating the surfactants, alkali is added to reduce surfactants' adsorption on a specific rock matrix. Many studies discuss anionic surfactant adsorption on the positively charged surface in sandstones and positively charged matrix in carbonate surfaces at neutral pH [29-35].

This study aims to do extensive research to evaluate surfactant, alkali, and salt's physiochemical properties at different concentrations. The study is based on finding the optimum point for surfactant, alkali, and salt with the help of design expert software. The software designs all concentration points for this work. Four different tests are performed with three materials: viscosity, pH, surface tension, and conductivity. The obtained optimum point will be used to see their effect on acidic crude oil. The results obtained from this work will better understand the impact of ionic materials in the EOR process and their interaction with the reservoir crude.

Procedure

Material

The cationic surfactant CTAB (cetyltrimethylammonium bromide), molecular weight 343.5 and purity 99 %, was purchased from Sigma Aldrich. The inorganic alkali NaOH (molecular weight 40) and KCl (molecular weight 74.5513), obtained from a central drug house (New Delhi). All the solution was prepared in in-house double distilled water, and all the experiments were performed at 30 0C. Berea sandstone (permeability 2.5 milliDarcy and porosity 0.19) and acidic crude oil (API 42.01) obtained from the Assam oil field were also used for wettability analysis.

Preparation of solution

The preparation of CTAB, NaOH, and KCl solution required extra care. All the solutions of different concentrations were made ready by dissolving a noted quantity of CTAB, NaOH, and KCl in distilled water with a specific conductivity of 1.3×10-6 S/cm under constant stirring for 1 hour. Twenty solutions are prepared for this experiment at different-different combinations of concentrations. All the varieties are obtained from the design expert software.

Methods

Viscosity measurement

The viscosity was measured using a suspended level capillary viscometer method, the requisite amount of solution used from solution to charge in a capillary to measure viscosity. Then the kinematic viscosity was calculated in terms of time and multiplied by the capillary constant. A known volume of empty pycnometer was taken, weigh and then filled with solution, then again weigh. The difference in the empty and filled pycnometer value gave the solution's mass value by using the following equation.

Dynamic viscosity = kinematic viscosity × density

The value of dynamic viscosity (cP) for all the solutions was calculated.

Surface tension measurement

The surface tension of the prepared solution was performed by using a ring tensiometer. The tensiometer was calibrated with distilled water before measuring the surface tension. The ring is made up of platinum, was cleaned before use. First, the ring is hanged and allowed to immerse into the solution, and then the amount of force needed to pull out the platinum ring from the solution is considered the surface tension. The surface tension data for each sample was repeated three times to achieve the reproducibility of results.

pH measurement

The pH is another important property for an ionic solution. The pH was measured by using Manti Lab MT 103 pH meter. The measuring rod of the pH meter was first appropriately washed with double distilled water and left to dry. The measuring rod of the pH meter was then put in the solution beaker and left for 5 minutes. Initially, the pH value increases or decreases according to the nature of the solution. After some time, the value becomes constant and then noted.

Conductivity Measurement

In this study, the solution's conductivity was measured by a Systronics Conductivity-TDS Meter 308, range 0.1 µS/cm to 100 mS/cm, accuracy ±1% of F.S. ±1 digit, India. A known amount of prepared solution of surfactants, alkali was added by using a micro-syringe. Then the measuring rod was left in contact with the sample at least for 5 min. In this way, the precise conductance of all the solutions was measured.

Selection of Design

All the experimental work was performed based on the concentration range obtained from the Design of Experiment (DoE). With these three selected materials, such as CTAB, NaOH, and KCl in wt%, we get the central composite design (CCD) of response surface methodology (RSM).

Table 1. Consisting of 20 experiments with different combinations as shown below was generated and the analysis of obtained data was done by using Analysis of Variance (ANOVA)

Std	A= CTAB (wt%)	B= NaOH (wt%)	C= KCl (wt%)	Viscosity (cP)	pH	Conductivity (mS/cm)	Surface Tension (dyne/cm)
1	0.1	0.1	0.1	2.57	11.79	5.72	52.9
2	1	0.1	0.1	2.084	11.11	6.18	52.4
3	0.1	0.5	0.1	2.157	12.31	22.5	52.3
4	1	0.5	0.1	2.441	12.2	22.1	52.8
5	0.1	0.1	0.5	2.287	12	11.79	52.1
6	1	0.1	0.5	2.423	12.01	12.98	50.4
7	0.1	0.5	0.5	2.086	12.42	32	50.6
8	1	0.5	0.5	2.415	12.4	30.7	50
9	-0.2069	0.3	0.3	2.259	11.99	18.68	51.7
10	1.3068	0.3	0.3	2.432	12.13	18.92	50.5
11	0.55	-0.0367	0.3	2.43	11.49	6.35	51
12	0.55	0.6364	0.3	2.182	12.18	33	49.5
13	0.55	0.3	-0.0364	2.091	12.12	14.53	52
14	0.55	0.3	0.6364	2.37	12.23	23.8	50
15	0.55	0.3	0.3	2.141	12.04	18.59	52.7
16	0.55	0.3	0.3	2.141	12.04	18.59	52.7
17	0.55	0.3	0.3	2.141	12.04	18.59	52.7
18	0.55	0.3	0.3	2.141	12.04	18.59	52.7
19	0.55	0.3	0.3	2.141	12.04	18.59	52.7
20	0.55	0.3	0.3	2.141	12.04	18.59	52.7

Results and Discussion

Optimization of the Physiochemical Characteristics of CTAB, NaOH, KCl Solution System

Viscosity Results

The viscosity highly depends on concentration and temperature, but in this case, the viscosity of the CTAB, NaOH, and KCl depends on each other's presence or concentration. In Figs. 2 and 3, the viscosity concerning concentration is represented. By ANOVA analysis for viscosity, some following results are drowned from Table 2.

Although, the p-value of the model is 0.0006, which is less than 0.05. The model value, which is less than or close to the 0.1 is considered significant. The significant value shows 95% confidence, i.e. 0.05 risk. The concentration of NaOH has the highest effect on the viscosity as compared to the other parameters. NaOH's p-value is 0.0132, which is less than the p-values of different parameters, namely CTAB (p-value 0.0339) and KCl (p-value 0.0854). All p-values of the parameters are less than 0.1, which shows that all three p-values of parameters are significant. So, the second significant parameter is CTAB. All the models are best fit like CTAB and NaOH (in Table A and B) shows the most significant value 0.0003 as any other combination. Their higher-order terms, A^2, B^2, and C^2, are also shown a good result.

Table 2. ANOVA statistics for viscosity of CTAB, NaOH and KCl

Source	Sum of Squares	Df	Mean Square	F Value	p-value Prob > F	
Model	0.409059	10	0.040906	11.3712	0.0006	**Significant**
A-CTAB	0.022469	1	0.022469	6.246134	0.0339	
B-NaOH	0.034066	1	0.034066	9.469923	0.0132	
C-KCl	0.013427	1	0.013427	3.732538	0.0854	
AB	0.115921	1	0.115921	32.22428	0.0003	
AC	0.055611	1	0.055611	15.45903	0.0034	
BC	0.002926	1	0.002926	0.813417	0.3906	
A^2	0.077369	1	0.077369	21.50745	0.0012	
B^2	0.050687	1	0.050687	14.0902	0.0045	
C^2	0.015327	1	0.015327	4.260797	0.0690	
ABC	0.041616	1	0.041616	11.56864	0.0079	
Residual	0.032376	9	0.003597			
Lack of Fit	0.032376	4	0.008094			
Pure Error	0	5	0			
Cor Total	0.441435	19				

Figs 1a, 1b, and 1c represent the viscosity of surfactant, alkali, and salt solution in terms of concentration. Fig. 1a, the viscosity of CTAB surfactant decreases with the concentration in the presence of a low concentration of NaOH and KCl (0.1 wt.%). The cationic charge of CTAB surfactant is neutralized by the anionic charge of NaOH and KCl, i.e. OH- and Cl- results in a decline in the surfactant viscosity. In Alkali and Salt's presence, the surfactant solution's viscosity rises because of the more number of molecules in the solution [36-37]. The same effect was also observed with the NaOH and KCl. Fig. 1b shows that the NaOH solution's viscosity decreases at a low concentration of CTAB and KCl and the same effect with the KCl at a low CTAB and NaOH concentration. The interaction between the molecules is the same as in Fig. 1a, and in all the cases, viscosity decreases.

The selected factors are show interacting nature, which can easily be seen in Figs 2a to 2f. From Figs 2a to 2c, the interaction of CTAB (A) with NaOH (B) is described at different values of KCl (C). It is found that at C = 0.1, 0.3, and 0.5 wt. As viscosity is increased as a more significant number of moles in the solution, and a decrease in B's viscosity is observed. The viscosity is less at a low concentration of A (0.1 wt.%) and a high B (0.5 wt.%) concentration. But on increasing the concentration of C, the interaction of A and B become more pronounced. At a high salt concentration, A and B's viscosity effect is more because of more significant salt molecules in the solution.

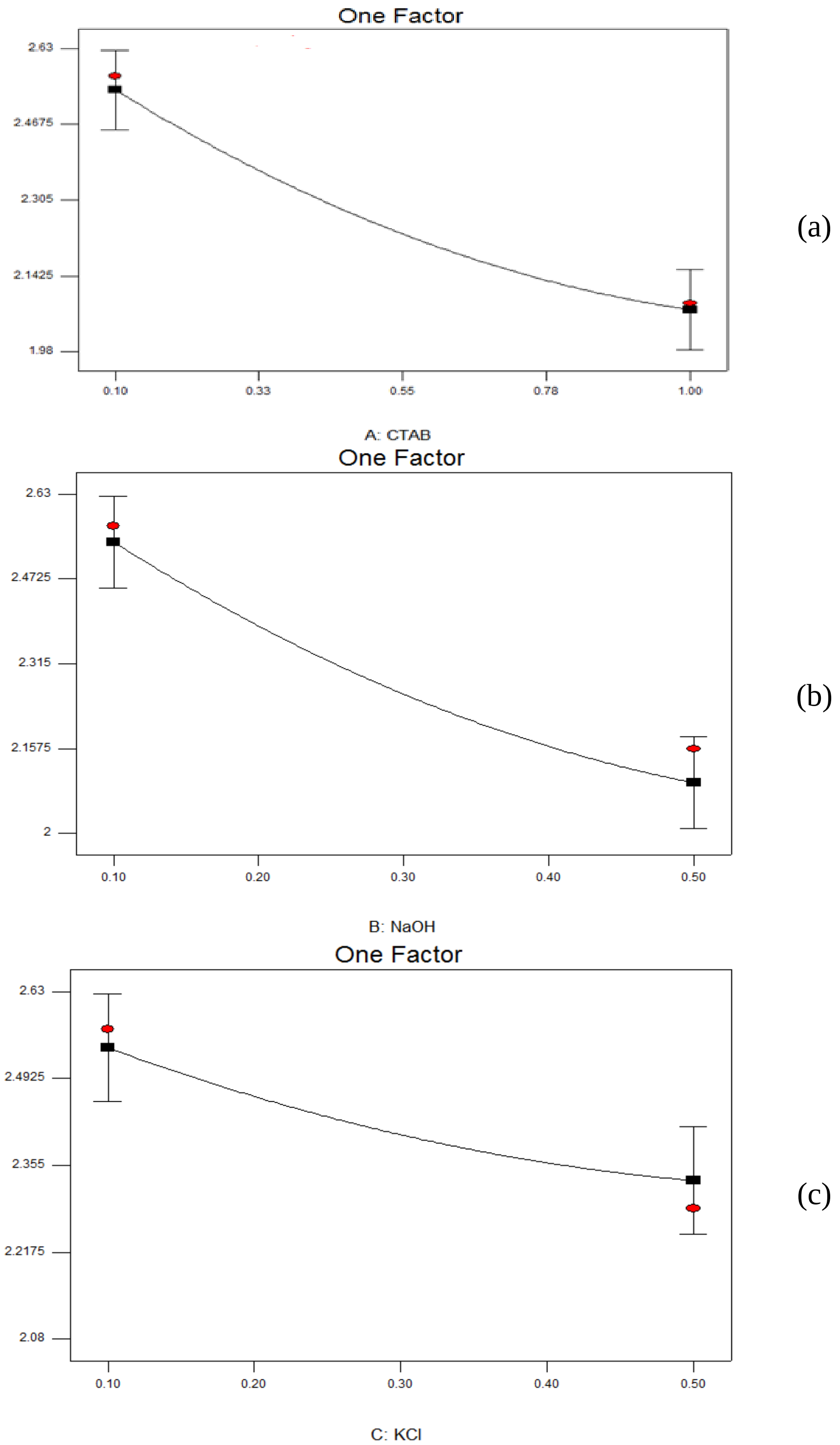


Fig. 1. Representation of single factor viscosity (cP) effect of (a) CTAB, (b) NaOH, and (c) KCL

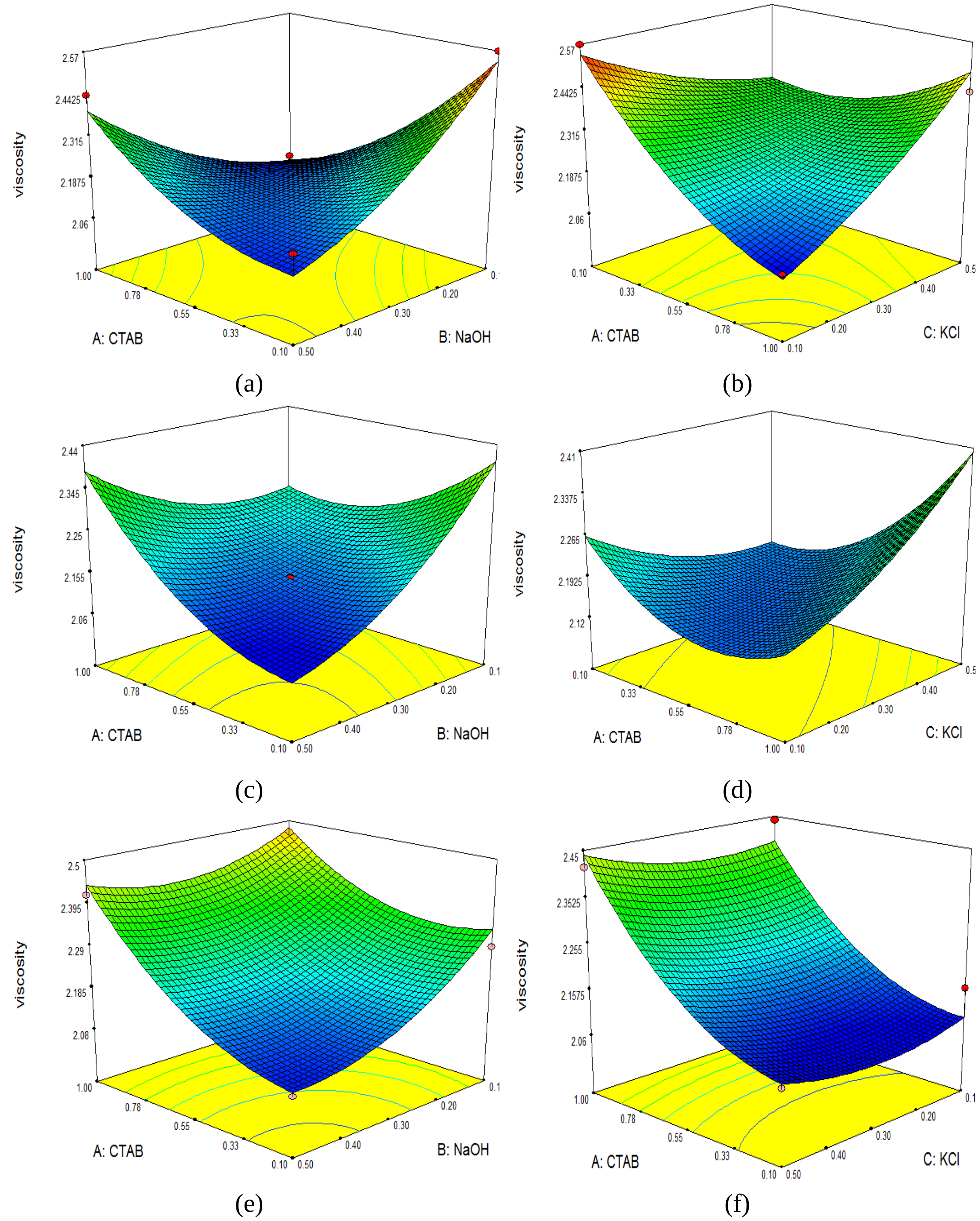


Fig. 2. Response surface plot for Viscosity (cP) of CTAB and NaOH at (a) 0.10 wt% of KCl, (b) 0.20 wt% of KCl, (c) 0.30 wt% of KCl. Also, CTAB and KCl at (d) 0.10 wt% of NaOH, (e) 0.20 wt% of NaOH, (f) 0.30 wt% NaOH.

From Figs 2d to 2f, the interaction of CTAB and KCl is studied. At a low concentration of alkali, the system's viscosity first decreases, and at a high concentration of alkali, the solution shows different behavior, and the observed viscosity is high. Suppose we want low viscosity for our system, the highest concentration of CTAB, and the lowest concentration of alkali and salt recommended. If we wish to high viscosity value for the system, a high concentration for all three parameters is recommended.

The resulting equation for the viscosity of CTAB, NaOH and KCl system:

Viscosity = 2.96428 – (1.3476×CTAB) – (2.39264×NaOH) – (1.35963×KCl) + (2.5395×CTAB×NaOH) + (2.12847×CTAB×KCl) + (1.72569×NaOH×KCl) + ($0.3618\times CTAB^{2}$) + ($1.48264\times NaOH^{2}$) + ($0.8153\times KCl^{2}$) – (4.00694×CTAB * NaOH×KCl) (1)

With this model equation's help, we can calculate the viscosity at any concentration of these components without experimenting.

Surface Tension Results

Surface tension can be lowered in a stable mixture of a brine-oil emulsion by alkaline flooding or surfactant alone. However, with the addition of surfactant into the alkali medium, a low surface tension value can be obtained compared to either alkali or surfactant unaided. According to Rudin et al. (1993), IFT can go through a deep minimum by optimizing the alkaline solution's pH [38].

Table 3. Surface tension for CTAB, NaOH and KCl in ANOVA statistics

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	21.40288	9	2.378098	6.27612	0.0041	**Significant**
A-CTAB	1.365353	1	1.365353	3.603351	0.0009	
B-NaOH	1.564728	1	1.564728	4.129527	0.0696	
C-KCl	8.326373	1	8.326373	21.97442	0.0869	
AB	0.55125	1	0.55125	1.454823	0.0255	
AC	0.66125	1	0.66125	1.745128	0.0215	
BC	0.36125	1	0.36125	0.953387	0.0519	
A^2	1.768913	1	1.768913	4.668399	0.0560	
B^2	6.105082	1	6.105082	16.11213	0.0025	
C^2	2.143945	1	2.143945	5.658159	0.0387	
Residual	3.789121	10	0.378912			
Lack of Fit	3.789121	5	0.757824			
Pure Error	0	5	0			
Cor Total	25.192	19				

In surface tension (dyne/cm), the model's p-value is 0.0041, which is less than 0.05 for significance. The p-value of CTAB (0.009) is more significant as compare to the NaOH (p-value 0.0696) and KCl (p-value 0.0869). This means the effect of CTAB on surface tension is more as compared to others. Except for CTAB, the higher-order terms of NaOH (B2) and KCl (C2) shows a more significant value of 0.0025 and 0.0560 in terms of surface tension. The smaller the p-value of any component, the higher the significant role in surface tension (Table 3).

Surfactants are the surface-active agent, which is used to lower the imbalance force between two phases. Figs. 3a to 3c, a decrease in the surface tension of CTAB, is observed, increasing the concentration of KCl (C). The surface tension value of CTAB decreases with KCl from 0.1 to 0.5 wt.% concentration because the addition of salt enhances the ionization in a solution due to the decrease in repulsive electrostatic force between the charges. The effect of alkali was also determined at different concentrations of KCl. In Figs. 3a to 3c, the surface tension values for the solution having alkali were smooth. Due to the unique property of NaOH, tolerate a low concentration of KCl salt. But at 0.3 wt.% of KCl, a small decline in NaOH's surface tension value was observed.

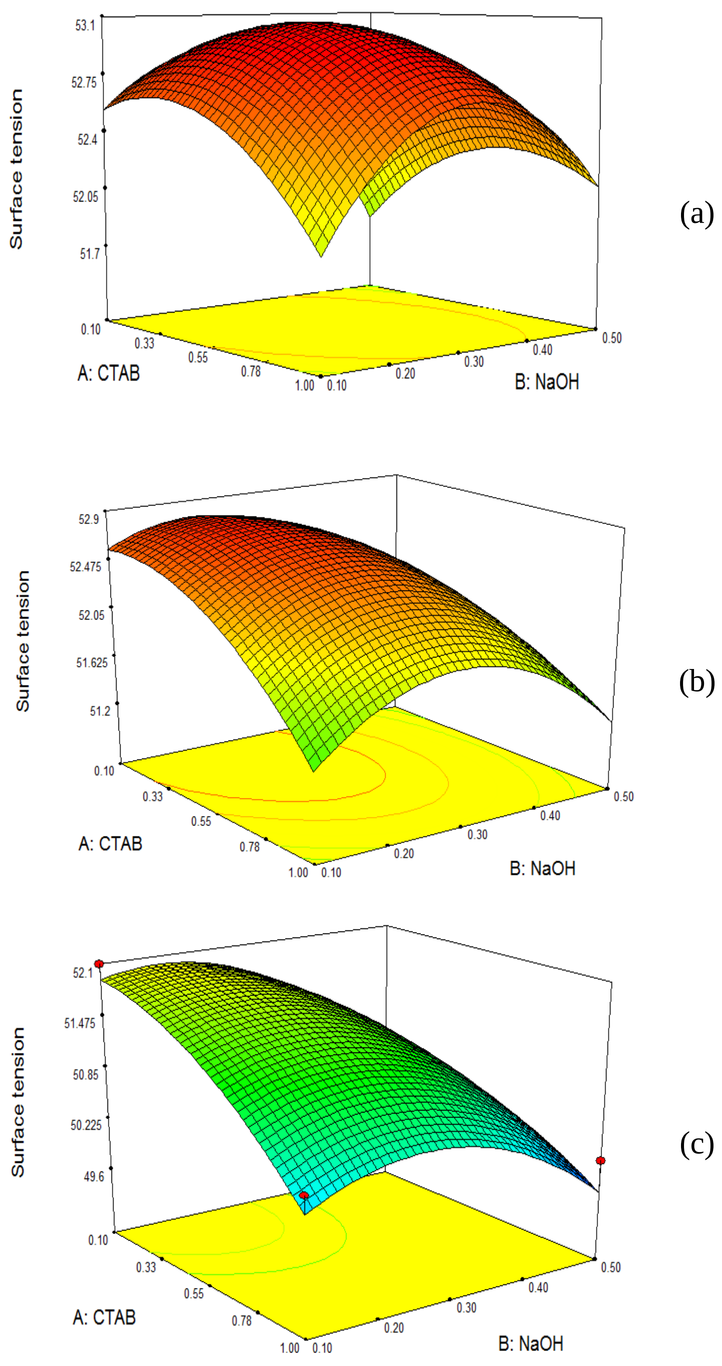
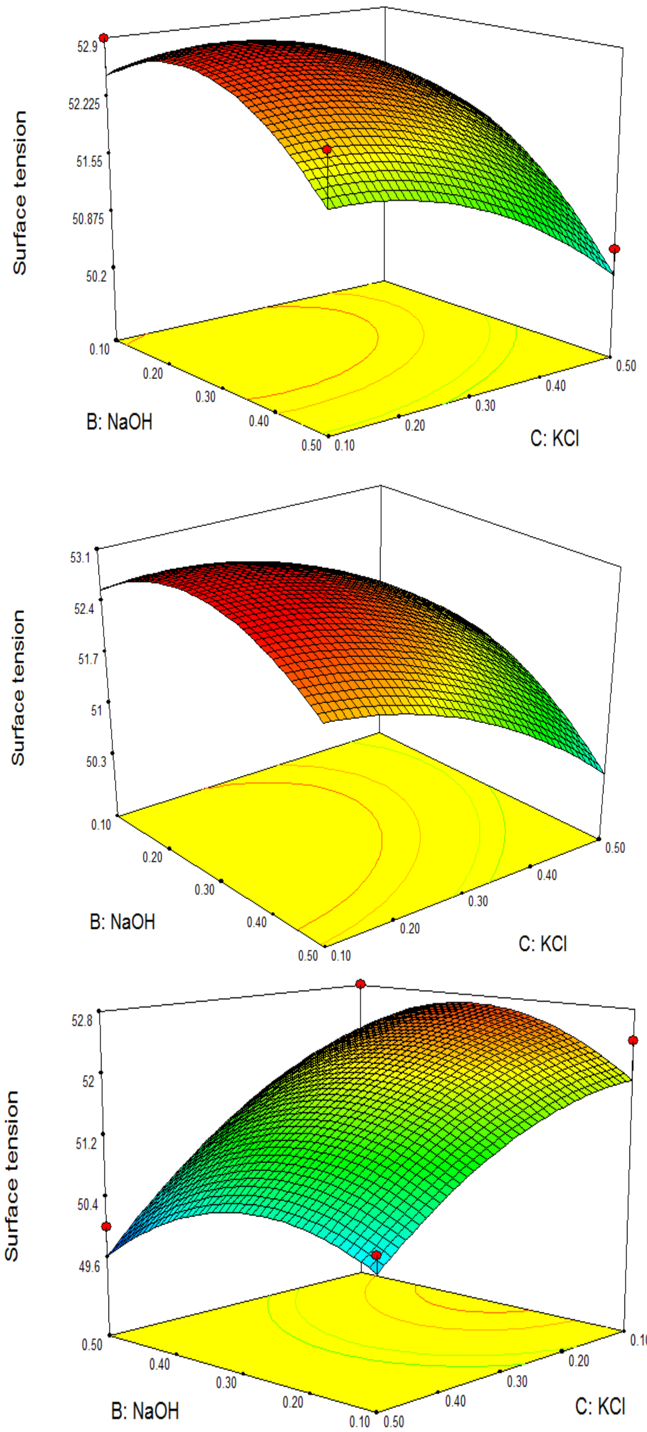


Fig. 3. Response surface plot for Surface Tension (dyne/cm) of CTAB and NaOH at (a) 0.10 wt% of KCl, (b) 0.20 wt% of KCl, (c) 0.30 wt% of KCl

(a)



(a)

(b)

(c)

Fig. 4. Response surface plot for surface tension (dyne/cm) of NaOH and KCl at (a) 0.10 wt% of CTAB, (b) 0.50 wt% of CTAB, (c) 1.0 wt.% of CTAB

From Figs. 4a to 4c, NaOH, and KCl are better at various concentrations of CTAB. The decreasing term is observed of NaOH and KCl surface tension value with CTAB concentration ranging from 0.10 to 1.0 wt.%. This low surface tension value proves a cooperative relationship between these three chemicals and their suitability for the surfactant-alkali flooding process [38-39]. Increasing the concentration of CTAB leads to enhance in the degree of ionization of charged particles. Thus, a decrease in surface tension value was observed. The final equation obtained for the surface tension of CTAB, NaOH and KCl system,

Surface tension = 51.35286 + (1.28382 × CTAB) + (8.06019 × NaOH +5.23216 × KCl) + (2.91667 × CTAB × NaOH) – (3.19444 × CTAB * KCl) – (5.31250 × NaOH×KCl) – (1.73012 × $CTAB^2$) – (16.27175 × $NaOH^2$) - (9.64263 × KCl^2) (2)

The obtained mathematical equation helps predict surface tension for the CTAB, NaOH, and KCl systems without experimenting. For example, if we want to observe the above combination's surface tension value at two wt.% of CTAB, 1.5 wt.% of NaOH, and 1.2 wt.% of KCl, we need to put these wt.% values in the equation to calculate the required surface tension values.

pH Results

This experiment shows that pH optimization is also essential as temperature and ionic strength in lowering tension force in the oil-brine system. The ionic stability of a solution is the measure of the ionic concentration. The higher the ionic strength of an alkali, the better it ionizes in water and its ability to form surfactant in-situ. This has been the basis of the interpretation of surfactant-enhanced alkaline flooding [40].

From Table 4, the p-value of the model is 0.0006, which is greater than 0.05, indicates that the model is significant. In this case, NaOH and KCl are considered substantial. Any value in Table 4, which is greater than 0.10 indicates the model is not significant, like CTAB (p-value 0.3571). AB, AC, and BC's interaction terms are also not substantial and exhibit a p-value is higher than 0.10.

Table 4. ANOVA statistics for pH of CTAB, NaOH and KCl

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	1.34315	6	0.223858	8.743682	0.0006	**significant**
A-CTAB	0.023337	1	0.023337	0.911536	0.3571	
B-NaOH	0.938688	1	0.938688	36.66422	< 0.0001	
C-KCl	0.188624	1	0.188624	7.36748	0.0177	
AB	0.03645	1	0.03645	1.4237	0.2541	
AC	0.07605	1	0.07605	2.970437	0.1085	
BC	0.08	1	0.08	3.12472	0.1006	
Residual	0.33283	13	0.025602			
Lack of Fit	0.33283	8	0.041604			
Pure Error	0	5	0			
Cor Total	1.67598	19				

The contour graph represents the results of CTAB and NaOH on pH. The graph's red region shows the highest pH value of NaOH at 0.5 wt.%, and there is no significant change in the pH value of CTAB with concentration. The light blue part of the graph shows the lowest value of the pH. But still, the pH value of the solution is more than 11.

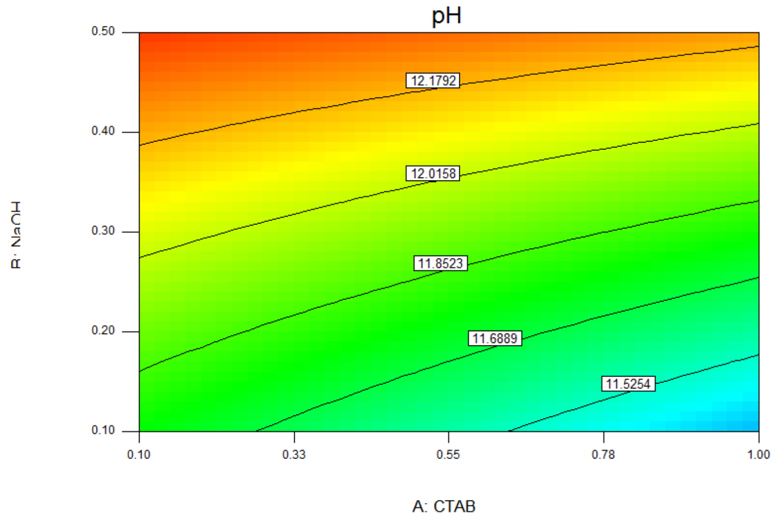


Fig. 5. Contour graph between the pH vs CTAB and NaOH concentration

From Fig. 6, on increasing NaOH concentration, the value of pH increases at 0.1 wt.% of KCl. At low salt concentration, a slight decrease in the pH of CTAB is observed. But on increasing the salt concentration ranging from 0.30 to 0.50 wt.%, there is a negligible change in the pH value of CTAB. The lowest pH value of CTAB at all concentrations is more significant than 11.5, which is a good indication for surfactant-alkaline flooding.

There is a significant increase in the pH value of NOH observed with concentration. At all KCl concentrations, the pH value of NaOH increased with increasing concentration. Further increasing the concentration means more ions in the solution, which results in a high pH value with high alkali concentration. A higher pH value indicates the solution is basic and has a better ability to react with acid present in the acidic crude reservoir. On the other hand, pH is generally a measure of OH- ions in the solution. The NaOH is dissolved in the solution and break into $Na^{+}$and OH^{-}. More number of OH^{-}ions present in the solution and the pH value will be higher on increasing NaOH concentrations.It also indicates that the higher the pH value, the retention of the surfactant on the rock is minimum. The rocks' wettability remains unchanged (water-absorbing properties); hence, spontaneous imbibitions are more efficient in recovering oil. A higher pH value indicates the solution is basic and has a better ability to react with acid present in the acidic crude reservoir. The presence of salt (salt) does not affect the nature of NaOH; this means NaOH offers salt tolerance ability. The red region of all the above three graphs shows that the combined effect of CTAB and NaOH at high concentration is high.

The resulting equation for pH of CTAB, NaOH and KCl system:

$$\textbf{pH} = 11.58948 - (0.64186 \times \text{CTAB}) + (1.64836 \times \text{NaOH}) + (0.74178 \times \text{KCl}) + (0.7500 \times \text{CTAB} \times \text{NaOH}) + (1.08333 \times \text{CTAB} \times \text{KCl}) - (2.50000 \times \text{NaOH} \times \text{KCl}) \quad (3)$$

With the help of the above equation, we can find the value of pH of any concentration.

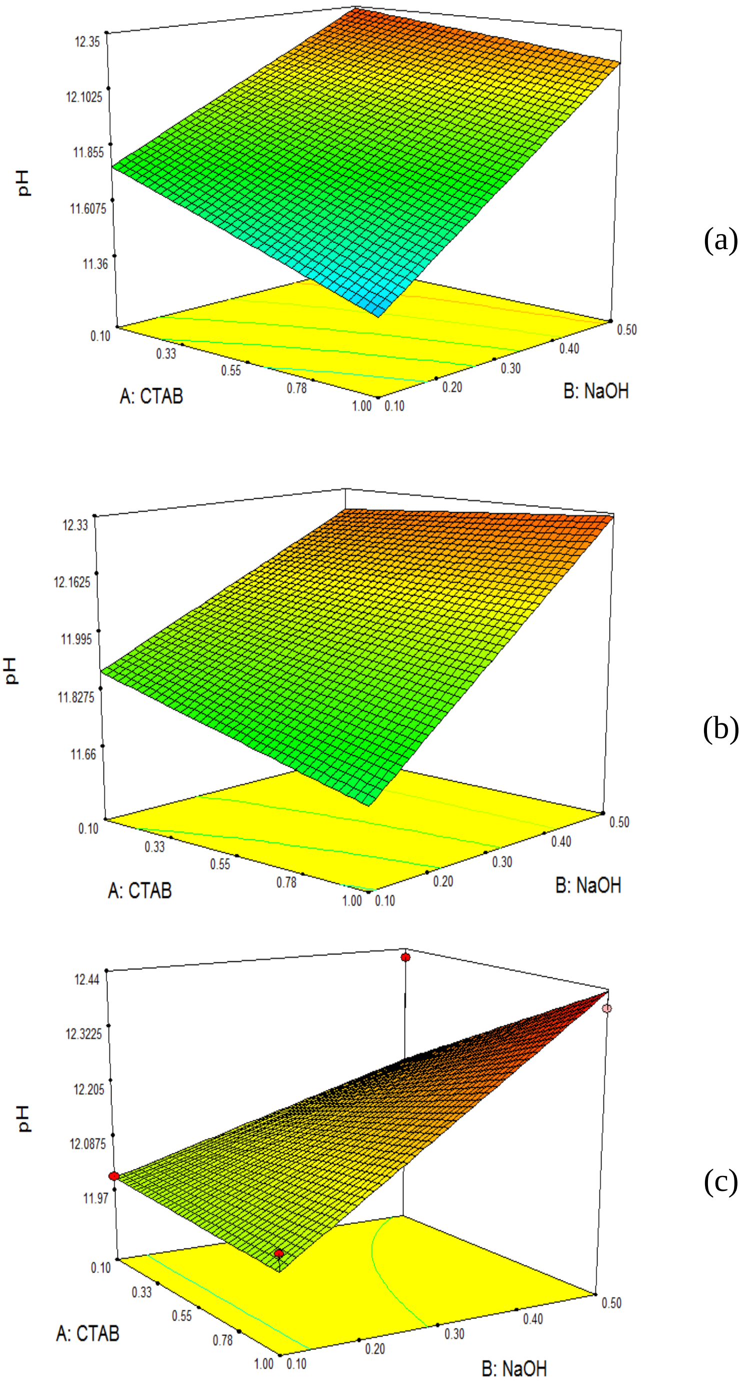


Fig. 6. Response surface plot for pH of CTAB and NaOH at (a) 0.10 wt% of KCl (b) 0.30 wt% of KCl (c) 0.50 wt% of CTAB

Conductivity Results

Conductivity to aqueous solutions is characterized by charge transfer affected by the presence of electrolytes and charged particles.

Table 5. ANOVA statistics for the Conductivity of CTAB, NaOH, and KCl.

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	1140.384	9	126.7093	103.6815	< 0.0001	**Significant**
A-CTAB	0.009157	1	0.009157	0.007493	0.9327	
B-NaOH	975.9679	1	975.9679	798.5981	< 0.0001	
C-KCl	158.7374	1	158.7374	129.8889	< 0.0001	
AB	1.402813	1	1.402813	1.147869	0.3092	
AC	0.003612	1	0.003612	0.002956	0.9577	
BC	3.419113	1	3.419113	2.797732	0.1253	
A^2	0.523356	1	0.523356	0.428243	0.5276	
B^2	0.203367	1	0.203367	0.166408	0.6919	
C^2	0.054542	1	0.054542	0.04463	0.8369	
Residual	12.22101	10	1.222101			
Lack of Fit	12.22101	5	2.444203			
Pure Error	0	5	0			
Cor Total	1152.605	19				

Model F value is 338.27 or p-value is 0.0001 suggested that the model is significant. There is a chance of 0.01 % that shows the model F value is at risk. The p-value of CTAB (A), its interactions AB, AC, BC, and higher-order terms A^2, $B^{2,}$ and C^2 is more than 0.05 suggested that the model is not significant. Only NaOH (B) and KCl (C) show a considerable value less than 0.05 (Table 5).

In the case of Fig. 7a and Fig. 8a, the conductivity (mS/cm) of CTAB at a low concentration of NaOH and KCl (0.1 wt.%) slightly increases with CTAB concentration. The transfer of charge particles of CTAB is not much as compared to NaOH and KCl. This is equivalent to a system where the bulk fluid is at rest, and particles move with their electrophoretic velocity. One can be converted into the other by adding a constant speed, and the system is electrically neutral, so there is no effect on the average conductivity. On the other hand, if the diffuse layer charge balances the particle surface charge, the double layer charge will be electrically neutral, which follows no significant change in the given solution's conductivity. In Figs. 7b, 7c, and 8, alkali and salt's conductivity increase with concentration. The effect of conductivity is more in the case of NaOH as compare to KCl at the same concentration range.

At 0.1 wt.% of CTAB and NaOH, the conductivity of KCl is also increased with concentration. The repulsion of co-ions from the double layer is observed due to a change in the solution's salt concentration. Also, in a solution, nonspecific adsorption changes the concentrations of co-ions and counter-ions by different amounts.

The resulting equation for conductivity of CTAB, NaOH and KCl system,

$$\textbf{Conductivity} = 1.31297 + (2.55939 \times CTAB) + (38.14209 \times NaOH) + (13.19600 \times KCl) - (4.65278 \times CTAB \times NaOH) - (0.23611 \times CTAB \times KCl) + (16.34375 \times NaOH \times KCl) - (0.94107 \times CTAB^2) + (2.96981 \times NaOH^2) - (1.53800 \times KCl^2) \quad (4)$$

Without performing any experiment, we can calculate the CTAB, NaOH, and KCl system's conductivity at any concentration.

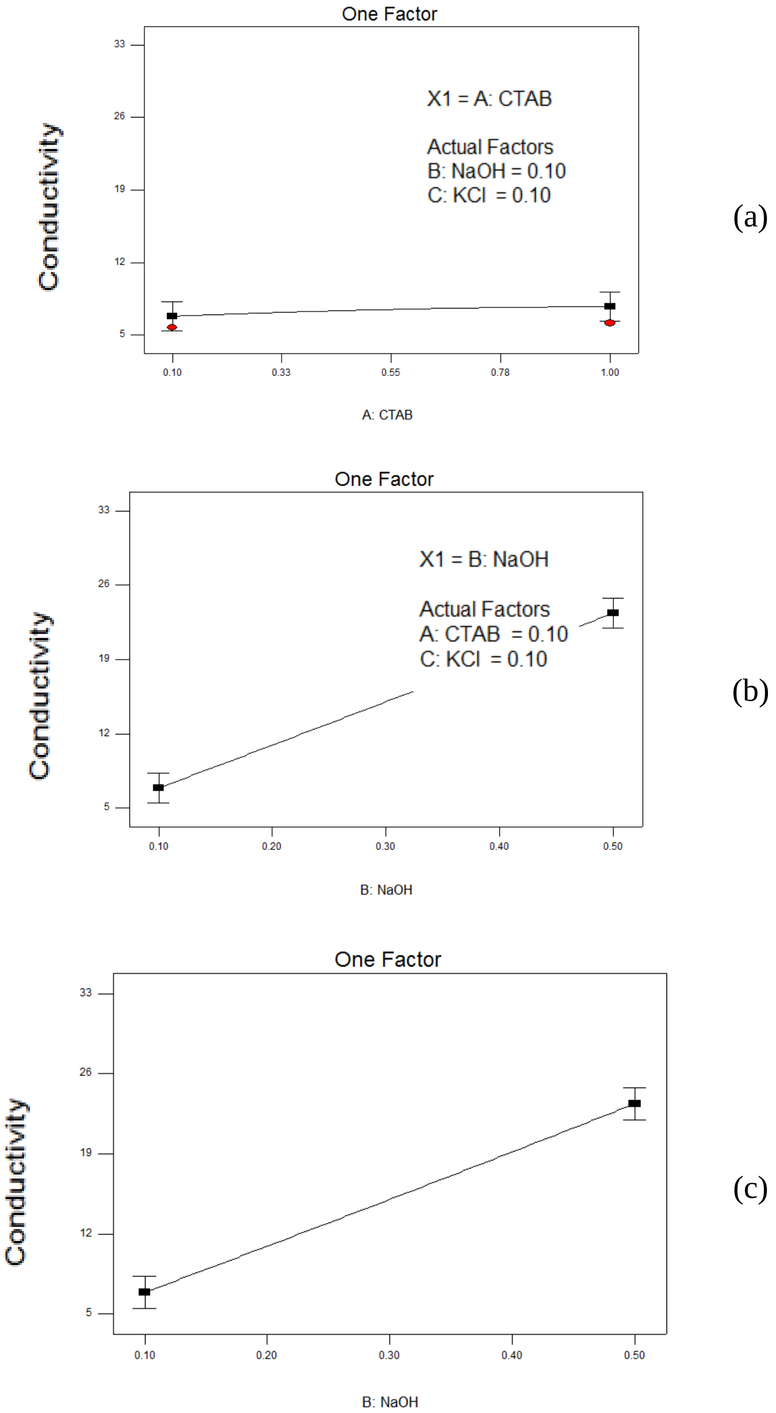


Fig. 7. Representation of single factor conductivity (mS/cm) effect of (a) CTAB, (b) NaOH and (c) KCl.

After analyzing all the responses (viscosity, surface tension, pH, and conductivity), it comes that the parameter selected should have a smaller value to maximize the responses by optimization process of ANOVA (analysis of variance) using design expert; the experiment number 8 is selected as an optimized concentration from Table 1. Hence, with the selected optimum point (experiment number 8), we measure this concentration point's effects on the acidic crude oil properties.

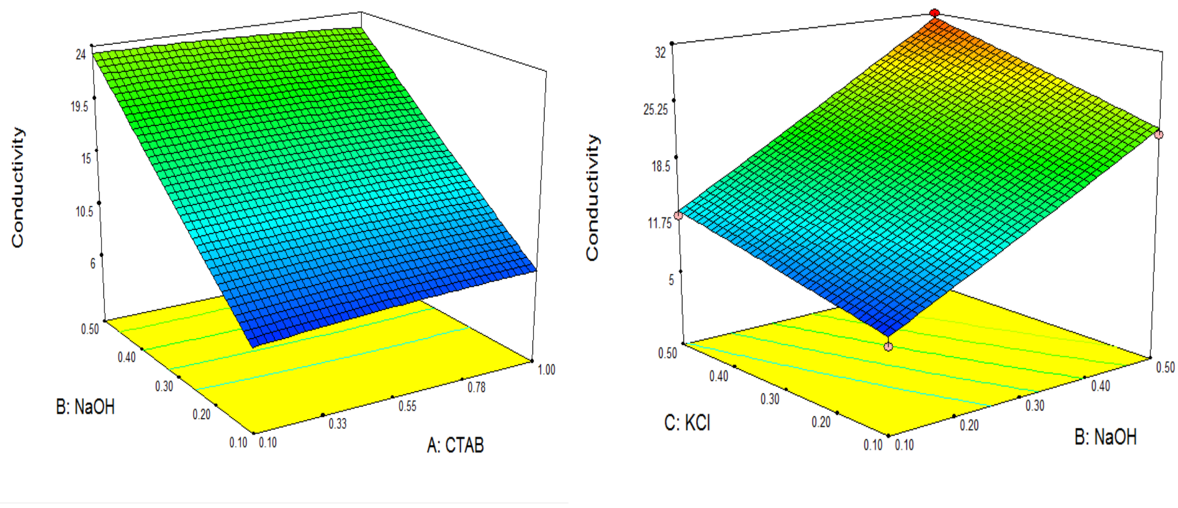


Fig. 8. Response surface plot for conductivity (mS/cm) of CTAB and NaOH and KCl.

Table 6 shows the maximization of points obtained from the data analysis after experiments by design experiment. The lower and upper limit show a selected concentration range before starting the investigation. The lower limit offers the lowest possible value for all four tests, and the upper limit is the highest potential value at all concentration range.

Table 6. Optimization of process conditions for viscosity, surface tension, pH and conductivity

Name	Goal	Lower Limit	Upper Limit	Lower Weight	Upper Weight
CTAB	is in range	0.1	1	1	1
NaOH	is in range	0.1	0.5	1	1
KCl	is in range	0.1	0.5	1	1
Viscosity	maximize	2.084	2.57	1	1
Surface tension	minimize	49.5	52.9	1	1
pH	maximize	11.11	12.42	1	1
Conductivity	maximize	5.72	33	1	1

Table 7, serial number 1, shows the maximum desirable limit (88 %) for all the parameters and responses. The desirability leads at the highest concentration, i.e. shows the optimum concentration value on changing the concentration; the desirability changes, increases or decreases with concentration (Fig. 9). So, a higher concentration value is recommended for further test with crude oil.

Table 7. Desirability values for viscosity, surface tension, pH and conductivity

Number	CTAB	NaOH	KCl	Viscosity	Surface tension	pH	Conductivity	Desirability
1	1	0.5	0.5	2.44039394	49.6099055	12.34256483	30.42367458	0.8817993841
2	1	0.5	0.5	2.439545271	49.6295845	12.34145919	30.39091493	0.8794640032

3	1	0.5	0.5	2.439422654	49.6252267	12.34253956	30.33591943	0.8793830836
4	0.99	0.5	0.5	2.436132378	49.62143279	12.34194596	30.42791929	0.8783078389
5	0.99	0.5	0.5	2.433478391	49.63007658	12.34147442	30.42769131	0.8759839639
6	1	0.5	0.5	2.437796754	49.65912357	12.34100219	30.24959504	0.8750516092
7	1	0.5	0.49	2.437342744	49.68097512	12.33855318	30.3047718	0.8733482436
8	1	0.5	0.48	2.433943559	49.76125404	12.33395694	30.16850827	0.8637448223
9	0.96	0.5	0.5	2.414579687	49.69123626	12.33806242	30.42553535	0.8592102351
10	0.89	0.5	0.49	2.36352658	49.91429731	12.32557467	30.29648156	0.806092802
11	1	0.5	0.41	2.408153221	50.42491386	12.29281837	28.94919596	0.7816557253
12	0.79	0.5	0.5	2.307168248	50.01868457	12.3163844	30.41607404	0.7547037324
13	1	0.5	0.38	2.400238495	50.66127729	12.27646492	28.46447195	0.7509878882
14	1	0.29	0.5	2.40302509	50.55766777	12.24956166	21.61251178	0.6918998146
15	1	0.21	0.5	2.422132307	50.54948457	12.17225299	18.31767221	0.6514548145
16	1	0.21	0.5	2.422928029	50.54640481	12.16974996	18.2252154	0.6504677178
17	1	0.5	0.28	2.382437199	51.39515253	12.21645546	26.68578755	0.6480968739
18	0.58	0.5	0.5	2.205493586	50.27727847	12.28987951	30.40391032	0.629624438
19	1	0.16	0.5	2.447164934	50.42042387	12.10196445	15.93571747	0.6269802659
20	1	0.13	0.5	2.463127904	50.31770913	12.06249178	14.75061205	0.6145180184
21	1	0.1	0.5	2.480591551	50.19542381	12.02190444	13.61617335	0.6013737387
22	1	0.5	0.1	2.391286019	52.15898386	12.11592643	23.68787747	0.513807755
23	1	0.5	0.1	2.39226405	52.17079749	12.11327865	23.60960192	0.5112585784
24	0.19	0.1	0.5	2.319842979	51.87156478	11.9168805	13.47429279	0.4003871353
25	0.12	0.1	0.5	2.322107173	51.9168546	11.91587858	13.65281756	0.398991934
26	0.11	0.11	0.5	2.322298625	51.92351186	11.91626154	13.69649312	0.3989894387

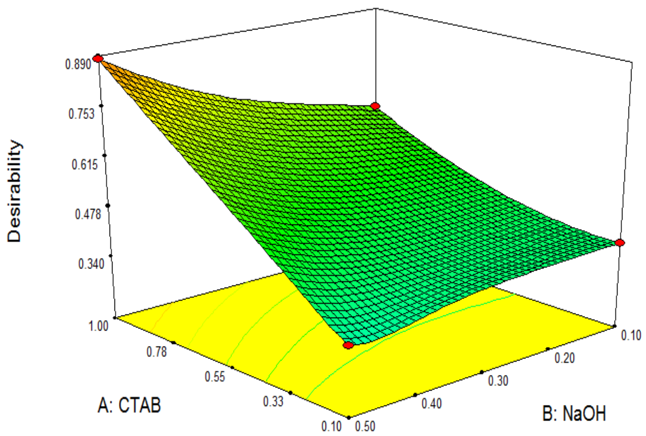


Fig. 9. Desirability response curve for all components at 0.5 wt.% of KCl

Effect of Optimum Point on Physiochemical Properties of Acidic Crude Oil

After obtaining the optimum value, we checked its effect on acidic crude oil properties by conducting several tests like viscosity, pH, surface tension, and conductivity. Results of the optimum point test are as follow:

Effect of Optimum Point on Crude Oil Viscosity

Before starting the viscosity experiment, we measure its API gravity value to know whether the crude is heavy or light. First, we estimate the density of crude oil by pycnometer. We use 50 ml of pycnometer and weigh it with and without the crude oil. The difference in its weight gives the value of mass, and the density was calculated by mass per unit volume. With the help of density, we find out specific gravity concerning standard fluid and then API gravity.

API gravity = (141.5 / sp. Gravity) – 131.5 = (141.5 / 0.8138) = 42.375
According to the API gravity the crude oil is light

For light and viscous crude oil, we have chosen a specific capillary tube. First, we measure the viscosity of oil by capillary tube viscometer. The viscosity of the acidic crude is 48.39 centipoise. We use the optimum point solution in a viscometer to calculate the optimum point on crude oil viscosity. The viscosity of crude oil decreases with optimum point concentration.

Viscosity of crude oil = 48.39 cP
Viscosity of crude oil with optimum point = 30.45 cP

The presence of CTAB surfactant and NaOH alkali is the main reason for the decline in crude oil's viscosity. The surfactant molecules adsorb on the crude oil's C-H chain and decrease the intermolecular force between them. The nature of the surfactant is to lower the imbalance force between two phases. Here it adsorbs on the surface of the C-H chain and lowers the force between the molecular chains. The presence of NaOH alkali enhances the performance of the surfactant. The acid present in a crude oil react with alkali and produces a surfactant by the in-situ saponification process. The produce soap work as a co-surfactant and a decrease in the value of crude viscosity was observed.

Effect of Optimum Point on Surface Tension

The same procedure was applied to measure crude oil's surface tension as we worked on in a previous test.The ring tensiometer was used for viscosity measurement, and the pull-out force is noted as surface tension. First, we examined the surface tension of crude oil without optimum point concentration. The crude oil surface tension is 64 dyne/cm. After adding the optimum point concentration, the surface tension of the oil decreases. The decrease in surface tension is observed due to the contribution from un-ionized acid to the surface tension, and then the scope of acid ionization is controlled by pH. As the concentration of acid increases, decreases in surface tension was observed. At the same time, the pH of the solution increases because of ionized acid.

Effect of Optimum Point on pH of Crude Oil

First, we measure the pH of the crude oil by using a pH meter. The pH of the crude oil is 6.2, which is less than 7. But also close to 7, this means the crude oil is acidic but not highly acidic. In the presence of an optimum point, we measure the pH again to know its effect on crude oil. The optimum point solution was prepared at a buffer pH of 12.2. At the optimum concentration of surfactant, alkali, and salt, the crude oil's pH is 10.12. As we already discussed above, in the case of surface tension, the acid ionization is governed by pH to lower the surface tension. An optimum pH exists where the surface tension is minimized [41-43].

Effect of Optimum Point on Conductivity of Acidic Crude

As we already discussed, the importance of the conductivity of crude oil in the above discussion. Here we applied the same concept as in the previous cases. First, we examine the conductivity of oil, and it was 40.2 µs/cm at 250C. Then we add optimum point concentration with crude oil and again measure the electrical conductivity. In the presence of an optimum point, crude oil's conductivity was 57.8 µs/cm at 250C. Because of the existence of ionic charge particles, the conductivity of crude oil increases. According to the results, only molecules involved in the charge transfer process are allowed the electron to pass through it. In aromatic compounds, the mechanism of charge transfer is governed by the weak cyclic π bound.

Conclusions

This article presents an experimental result that was carried out to find the optimum point's value and its effect on the acidic crude oil. A range of combinations of concentrations was evaluating to characterize their interaction with each other and their interaction with the acidic crude oil. At a low salt concentration, CTAB and NaOH's viscosity decreases due to the neutralization of opposite ionic charges of each other. But, at a high salt concentration, CTAB and NaOH's viscosity effect is more due to the more significant number of salt molecules in the solution. Hence, the solution's viscosity increases. Also, the surface tension in the case of CTAB surfactant decreases the concentration of KCl, ranging from 0.10 to 0.50 wt % because the addition of salt enhances the ionization in a solution. The formation of micelles takes place on further increasing the concentration of surfactant. The presence of salt facilitates the formation of the micelles in the solution, and the value of surface tension decreases. At all KCl values, the pH value of the surfactant solution does not much effect.

pH is generally a measure of OH^- ions in the solution. The NaOH is dissolved in the solution and break into Na^+ and OH^-, leading to more hydrogen ions in the solution. The conductivity of the electrolyte solution also shows a significant effect. The effect of the KCl was studied, and the presence of KCl in the solution causes the repulsion of co-ions from the electric double layer. The optimum point on crude oil is very significant and shows excellent results, which is very useful in studying crude property and enhances oil recovery.

Nomenclature

API	Americal petroleum index
ANOVA	Analysis of variance
CTAB	Cetyltrimethylammonium bromide
cP	Centi poise
IFT	Interfacial tension
KCl	Potassium chloride
mS/cm	Milli Siemen per centimeter
NaOH	Sodium hydroxide

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