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The Effect of Active substance in the crude oil on the Interfacial Tension[1]

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Abstract: The effect of active substance on the interfacial tension of an alkali/inorganic salt/synthetic surfactants/ crude oil system was studied, through the ways of contact time, infrared scan and mass analysis. This system consisted of heavy alkyl benzene sulfonate, sodium chloride, sodium hydrate and Daqing crude oil. The result of the experiment indicate that active substance diffusion from oil/aqueous interface to aqueous phase and finally the process of diffusion has a equilibrium in the system with the prolonging of the contact time. At the same time,the value of the minimum IFT and the value of equilibrium IFT rises with the prolonging of the contact time and has a linear relationship between IFT and t-1/2 when IFT value approaching the minimum and after the minimum, the process is diffusion controlled. The oil and aqueous phase had been analysed by infrared scan and mass analysis, and then the phenomenon have been found that the content of active substance in the oil decreased and the content of active substance in the aqueous increased after alkali had a reaction with compound system. It is proved that the active substances in the oil play a very important role for reducing the IFT.
Key words: contact time; diffusion action; alkali; interfacial tension

1. INTRODUCTION

Alkaline-surfactant-polymer (ASP) flooding is a technique that is used in several different oil field in China to enhance oil recovery, especially in the Daqing and Shengli during the past few years. Alkali can

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reacts with the acidic substances in crude oil and form interfacially active componets that accumulate at the oil/aqueous interface. Surfactant can reduce the interfacial tension of the oil/aqueous interface. And polymer has the ability of increasing the viscosity of displacement fluid. Even though the ASP flooding increases the oil production compared to the water flooding techniques, it is faced with new problems. The production fluids form stable oil-in-water emulsion and formation scaling is the primary type of formation damage in water injection of oilfield, which severely influences economic effect. It is believed that the alkali added in the compound system cause those problems. It becomes very important that the effect of acidic substance in the crude oil on the interfacial tension.

In 1973, Foster studied the relation between the capillary number ($\mu v/\sigma$) and the oil recovery. And it is pointed that the residual oil saturation would be close to zero when the capillary number achieves the amount of 10^{-2}.[5] The interfacial tension must reduce to 10^{-3}mN/m in order to make the capillary number achieve the amount of 10^{-2}. In 1995, using the Linear Berea Sandstone core, Taglor and co-workers have carried out the alkali flooding experiment, in which surfactant was added to alkali. And the results show that the correlation between the displacement efficiency and the minimum dynamic IFT is better than the equilibrium IFT [2-4]. Youssef Touhami got the same conclusion in 2001.[6] So the study on the dynamic IFT between oil and displacing fluid is essential to chemical flooding.

The oil/water IFT could reduce to an ultra low value due to the synergistic effect of alkali and surfactant, which makes ASP flooding become a focus of EOR research. Many interests have been focused on different aspects of alkali concentration, ironic intensity and surfactant conformation on the oil/water IFT [6-14], but they ignored that the displacing process is a dynamic process, with a long contact and reaction between oil and displacing fluid. In most cases, the IFT property of oil and the displacing fluid is not the same as the experiment result in the reservoir. The reason is that the contact time, as well as other factors of the reservoir such as pressure and temperature, will influence the IFT property. However, it still has not been studied systematically about how IFT will change with time and how much it will change. In this paper, the concept of contact time is proposed and correlative experiments are designed to study it. Regarding to this point, the important influence of the contact time of oil and surfactant on the IFT of the compound system is studied through systematical experiments, which provides a proof for the effect of alkali on the ASP flooding, and the selection of the formula of ASP system.

2. EXPERIMENTAL

2.1 Materials

Heavy alkyl benzene sulfonate (HABS), used as a surfactant, was provided by Daqing Oilfield Research Center;

NaOH, NaCl and Prokpanone are analytical grade reagents and purchased from Beijing Chemical Reagents Company. 1.5% NaOH, 0.3% NaCl and 0.2% HABS solutions were prepared with distilled water.

Daqing crude oil, degassed and dewatered, with a acid value of 0.06mg KOH/g oil, density of 0.96075g/m^3, viscosity of 9.80mPa·s at 25 ºC ,was provided by the First Oil Production Factory, Daqing Oilfield.

[5] Foster. M. R.. A Low-Tension Water Flooding Process.Mobil Research and Development Corp:1973(Feb).SPE:3803

[6] Youssef Touhami, Dipak Rana. Vladimir Hornof. Effects of Added Surfactant on the Dynamic Interfacial Tension Behavior of Acidic Oil/Alkaline Systems. *Journal of Colloid and Interface Science*, 2001, 239:226–229.

2.2 Apparatus

TEXAS-500 interfacial tensiometer, made in America. AY120 automatic electronic balance, made in Japan. Quattro Premier XE mass spectrometer, made in Waters company. Nicolet company Nexsus670 FTIR infrared spectrometer, made in America.

2.3 Experimental procedure

With a microsyringe, oil droplet was injected into the glass tube (Φ5mm) that was already filled with the multisystem of NaCl 1.5%,NaOH 0.3% and HABS0.2%. The volume of the oil droplet is about 2μL. The volume of the glass tube is about 0.29mL. At the same time it must make sure that the oil droplet can contact well with the compound system. Then the tube was put in an incubator with the temperature of 45℃. After a certain contact time(T'), such as 0 minutes, 40 minutes,60 minutes,120 minutes,300 minutes and 1440 minutes, the tube was taken out, and the dynamic IFT would be measured by interfacial tensiometer.

3. RESULTS AND DISCUSSION

3.1 Influence of contact time on dynamic interfacial tension

Contact time is defined as the contact time of oil with displacing fluid under reservoir conditions (pressure and temperature). As pressure has a slight effect on interfacial tension, it is not considered here. Because of reservoir temperature is constant(45℃), temperature is not considered here. Fig 1 shows that interfacial tension can be ultra low when the contact time is between 0~60 minutes. While it will be higher than 10^{-2}mN/m when the contact time exceeds 120 minutes. Additionally, when the contact time ranges from 0 minutes to 60 minutes, the minimum IFT is obviously lower than the value of equilibrium IFT. The curve firstly falls and then rises. With the prolonging of time, the ratio of the minimum IFT and the equilibrium value gradually increases and is close to 1(Table 1). And the curve is more and more smooth.

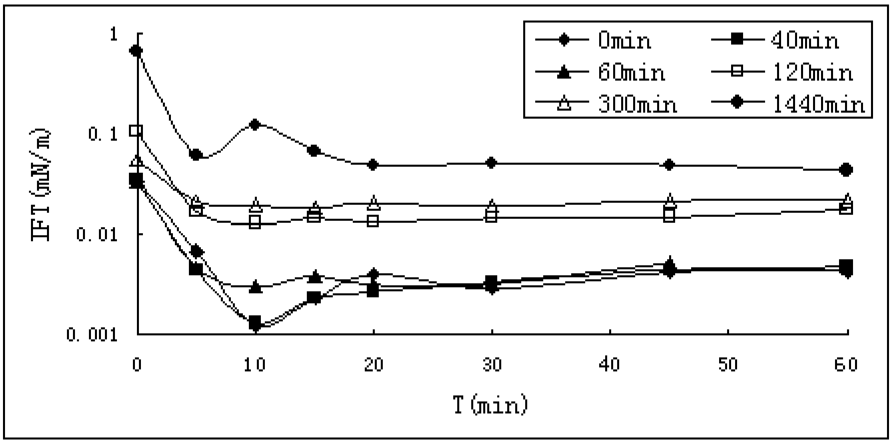


Fig. 1. Relation between Dynamic IFT and Contact Time

Table 1. Ratio of Minimum IFT and Equilibrium Value

contact time, min	IFTmin,mN/m	IFTequ,mN/m	Ratio
0	1.2×10^{-3}	4.2×10^{-3}	0.28
40	1.3×10^{-3}	4.7×10^{-3}	0.28
60	3.0×10^{-3}	5.2×10^{-3}	0.58
120	1.3×10^{-2}	1.7×10^{-2}	0.76
300	1.8×10^{-2}	2.1×10^{-2}	0.86
1440	4.8×10^{-2}	4.8×10^{-2}	1.00

3.2 Influence of contact time on minimum IFT and equilibrium value

As shown in Fig 2, the minimum value of IFT rises with the increasing of the contact time. When the contact time varies from 0 minutes to 1440 minutes, the minimum IFT will rise from 1.2×10^{-3}mN/m to 4.8×10^{-2}mN/m, and the curve between IFT and contact time is linear relationship The equilibrium value of IFT increases smoothly with the increasing of contact time. And it maintains almost unchanged during the first 120 minutes. After 120 minutes, it will go above 0.01mN/m and increase smoothly.

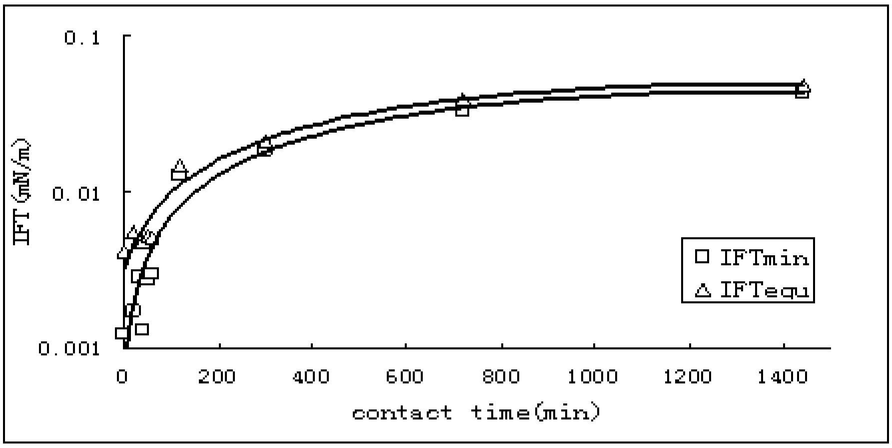


Fig. 2. Relation between IFT and contact Time

If we put the compound system singly in the incubator with a temperature of 45℃ for 1440 minutes, then take it out, and add the oil droplet into it. After the measurement, we can see that the IFT achieves the normal system (Fig.3). This indicates that the interfacial property of the compound system does not change by its own. It is the contact time that influences the IFT.

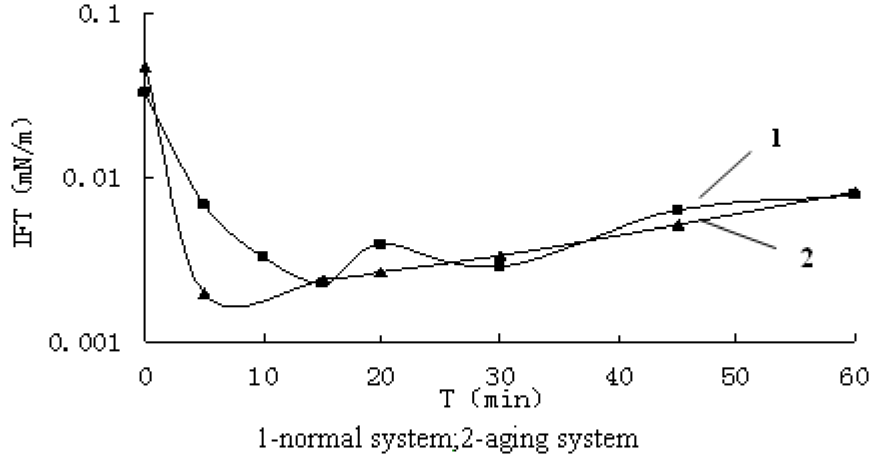


Fig. 3. IFT Comparison before and after Aging

3.3 Influence of contact time on dynamic interfacial tension of straight kerosene

If oil phase has been replaced by pure straight kerosene, which other parameters do not change , the result of the experiment will be different. From the Fig 4, we can see that the ratio of the minimum IFT and the equilibrium value is close to 1.and don't varies with the contact time. Because the content of the acidic and active substances in the straight kerosene is too low, alkali can not has a very important role on it. As is shown in Fig 5 ,we can have a result more clearly than before that the value of them both FTmin and IFTequ are slightly increased with contact time and rising amplitude is very little.

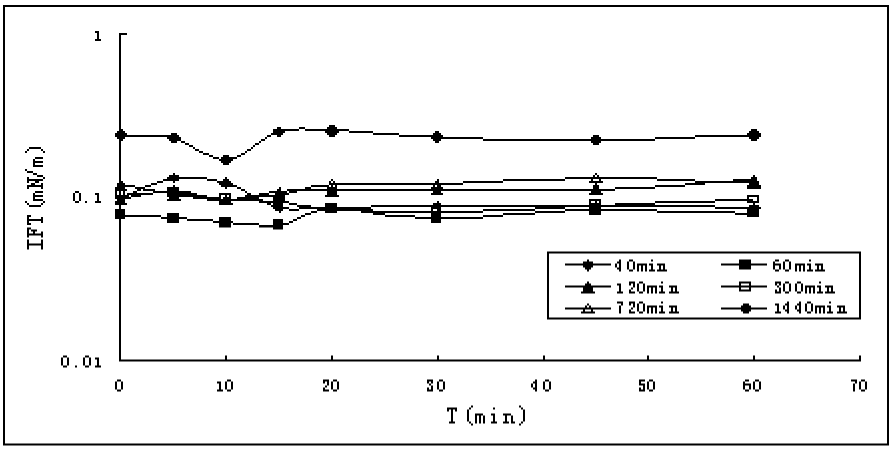


Fig. 4. Relation between Dynamic IFT and Contact Time

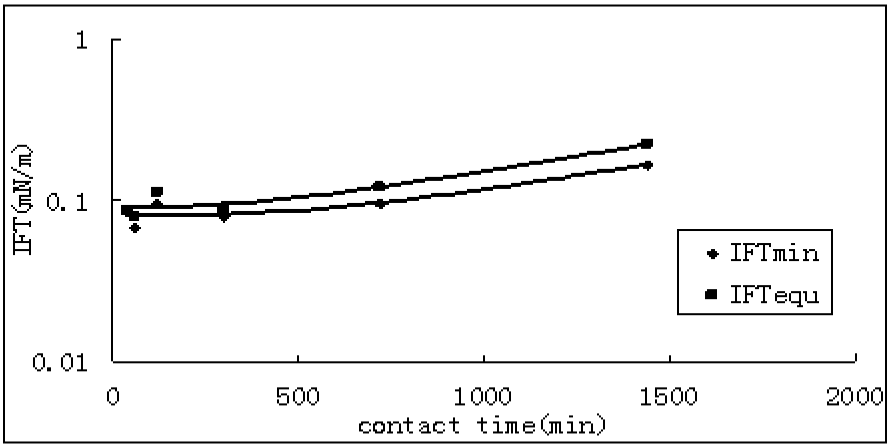


Fig. 5. Relation between IFT and contact Time

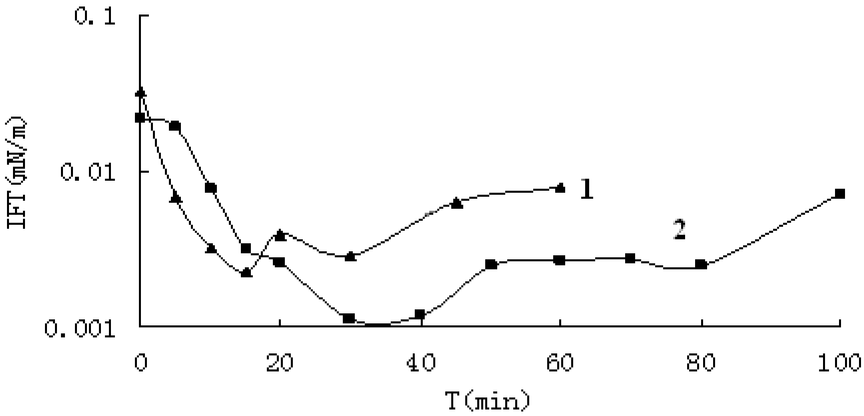
Base on the result of the experiment , we can infer that there will be two reasons for the above phenomenon, one is that the acidic-active substances of the oil react with alkali and generate the surfactant of oil by itself which could be expressed by $RCOO^-$[15] . Using RCOOH expresses the acidic-active substances of the oil. The amount of [$RCOO^-$] is small but it can help the applied surfactant of the compound system adhere to the oil/water interface well. At the same time the value of the [RCOOH]/[$RCOO^-$] decreases, thus it will make the IFT decrease and achieves IFT minimum at last. However, with the prolonging of the contact time, the value of the [RCOOH]/[$RCOO^-$] achieves a dynamic balance. So the ratio of the minimum of IFT and the equilibrium value gradually increases and is close to 1.With the increasing of the contact time, the RCOOH of the oil is continuously consumed and used up at last. At the same time, the $RCOO^-$ diffuses gradually into the surrounding solution. At last, the generated surfactant achieves a dynamic balance with a minimum adsorption at the oil/water interface. It is just the diffusion from the interface into the surrounding solution that makes the minimum IFT increase gradually.

The other reason lies in that there are also other materials like wax, asphalt and gum, which play a very important part in the formation and stabilization of the oil/water interface film.[7] Due to the low concentration of alkali, it can not damage the formed interface effectively. Thus it can not further stretch the oil drops. So it eventually influences the arrangement of the surfactant on the interface, and the IFT tends to be stable.

3.4 Test of the active substance of oil

In order to test the function of the active substance of oil, oil of 30mL was added into compound system of 60mL (NaCl 1.5%, NaOH 0.3%). On the precondition of non emulsification, they were mixed round and hold up for 24 hours. Then the solution of 20mL was taken out. Through filtration, HABS with a concentration of 0.2% was added to it. We call this solution the compound system enriched of surfactant of oil. Then the IFT between it and oil was measured. Fig. 6 shows the results.

[7] Lin M. Q.,Yang H. S., Qiao A. J., *et al.* Active Components and Interfacial Activity of Daqing Crude Oil. *Journal of the University of Petroleum*, 2003, Vol 27(93-95)(in Chinese)



1- normal system;2-rich active substance system

Fig. 6. Relation between Minimum IFT and Pre-contact Time

The time scope that ultra low IFT is achieved in Curve2 (10min to 80 min) is obviously larger than that of Curve1. Moreover, the minimum value and the equilibrium value are much lower than the normal system. The reason is that the system of Curve 2 represented has contacted with plenty of oil in advance and has generated much surfactant of oil by itself. Thus the concentration of the surfactant is much higher than the normal system. So the surfactant can be well adsorbed on the oil/water interface. To a large extent, it helps the applied surfactant to reduce the IFT and maintains the minimum IFT value for a long period.

Oil droplet was smeared on the slice of potassium bromide. It will be compared with the oil droplet that was smeared on the same type slice but already had contacted well with the compound system. Then through the infrared scan, there are some difference between them. As Fig 7 and Fig 8 show, absorption peak of organic acid at 1699, 1602 and 2672 cm-1 weakened. The ratio of the absorption peak of organic acid at 1701.50 cm^{-1} and absorption peak of methane at 1462.37 cm^{-1} can reflect the change of the organic acid in oil droplet. The ratio of normal oil droplet is 0.5/6.5=0.077, but the ration of oil droplet that contact well with the compound system is 0.2/4.9=0.041. The experiment result shows that content of organic acid decrease after contact with compound system. At the same time, the absorption peak of carboxylic acid at 1576 cm^{-1} has been found in the displacement fluid of the compound system. (Fig. 9) It indicate that some organic acid transform into organic acid salt. The solid composition of the displacement fluid can be extracted by poropanone. Through the infrared scan and mass analysis, some organic acid salt and phenolics have been found.(Fig. 10 and Fig. 11)

This has proved that the active substances of oil have a key effect on reducing the IFT. However, this effect may not be the decisive one as some people thought formerly. Alkali reacts with the active substance of the oil and generates new surfactant in site. Thus it helps the artificial surfactant reduce the IFT well. To illustrate this phenomenon, we could also add some adjuvants that have similar property with the surfactant. And we can get the same result.

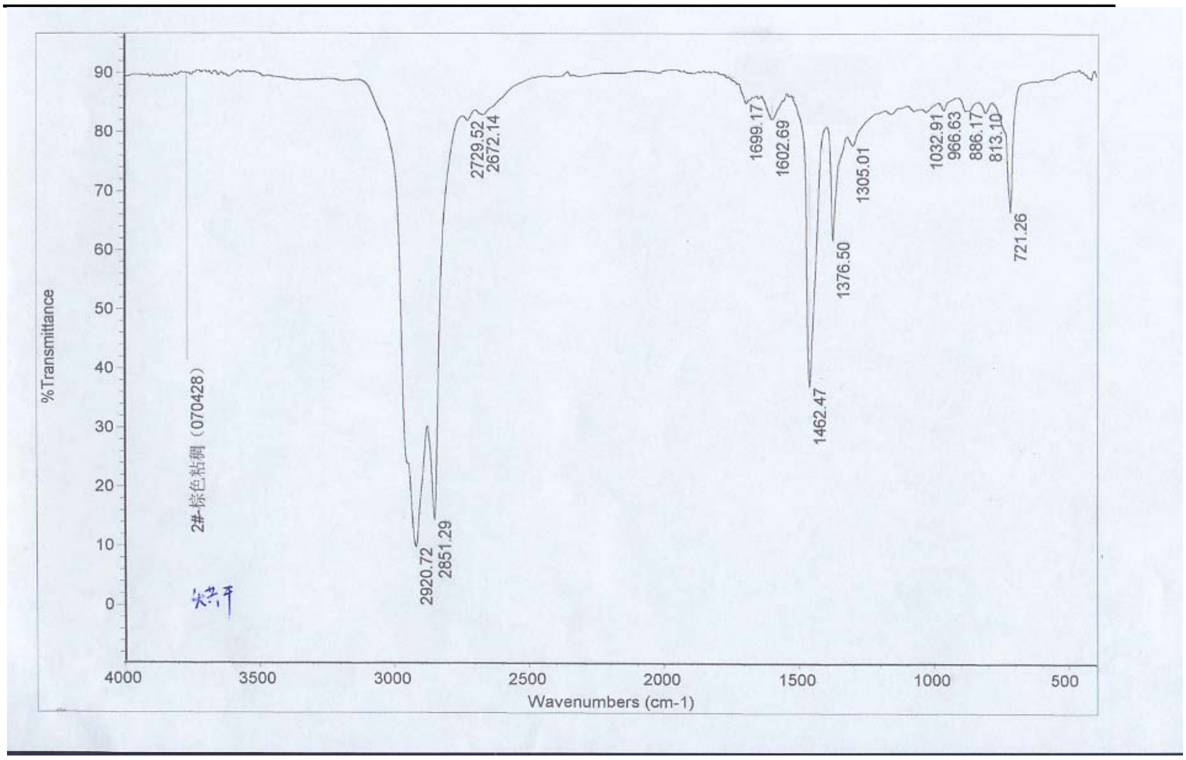


Fig. 7. The IR spectra of the normal crude oil

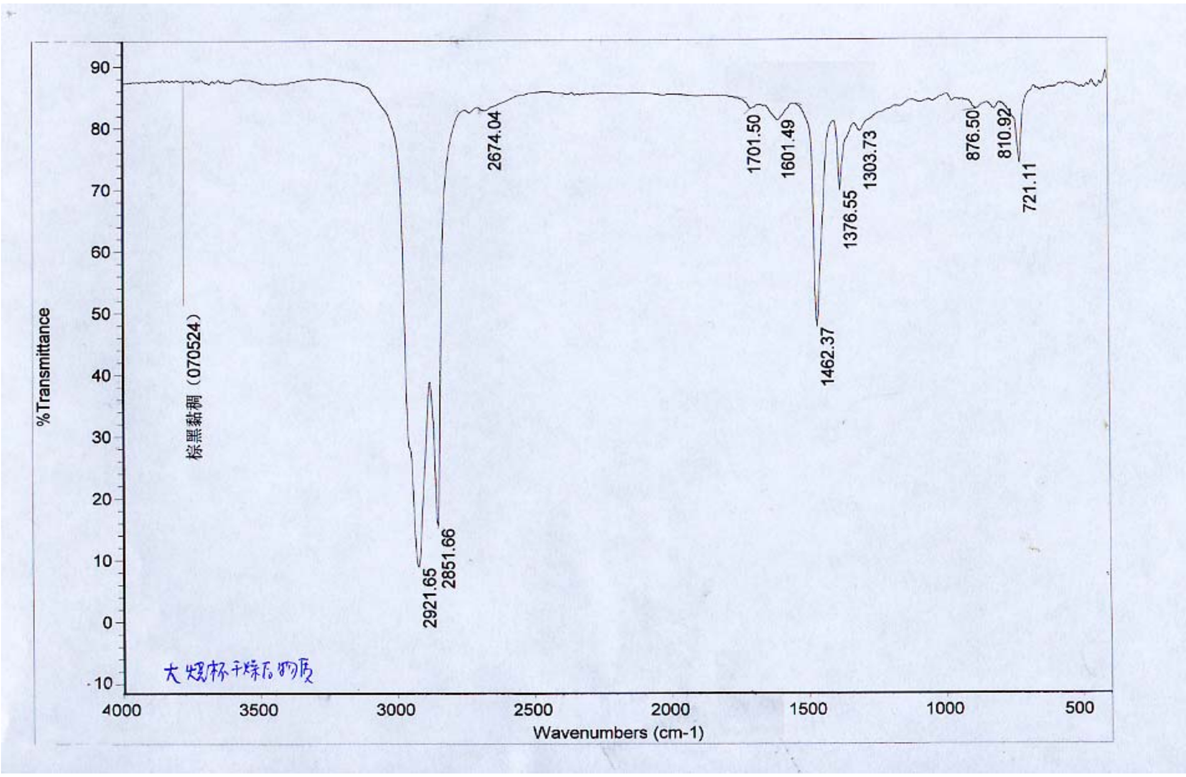


Fig. 8. The IR spectra of the crude oil that contact well with compound system

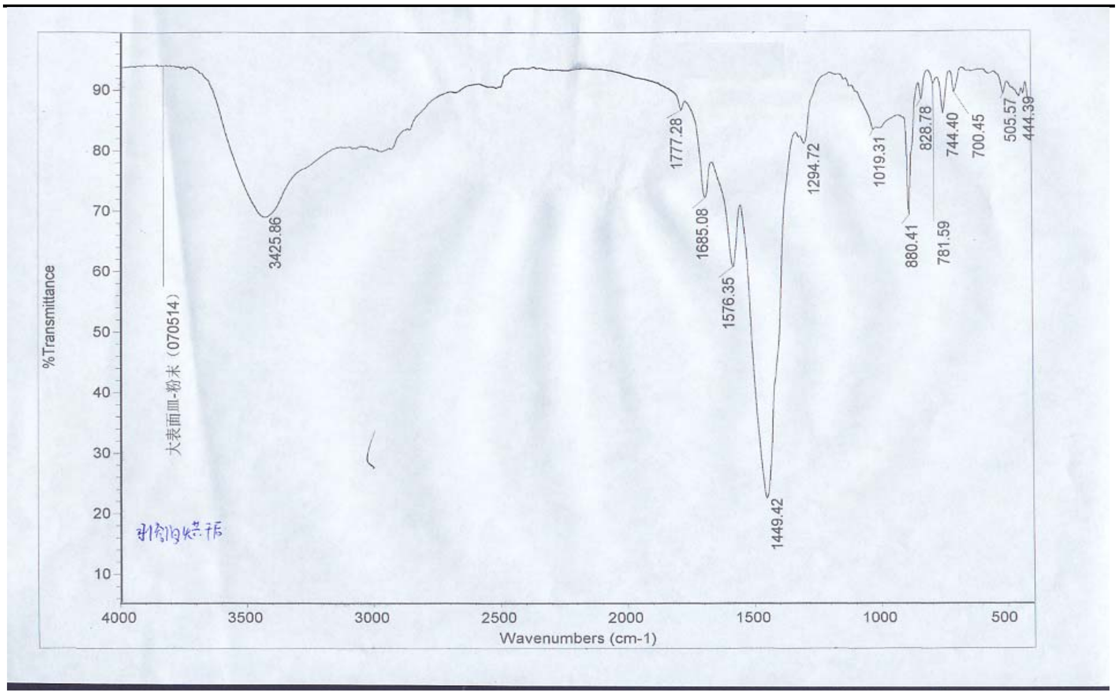


Fig. 9. The IR spectra of the displacement fluid

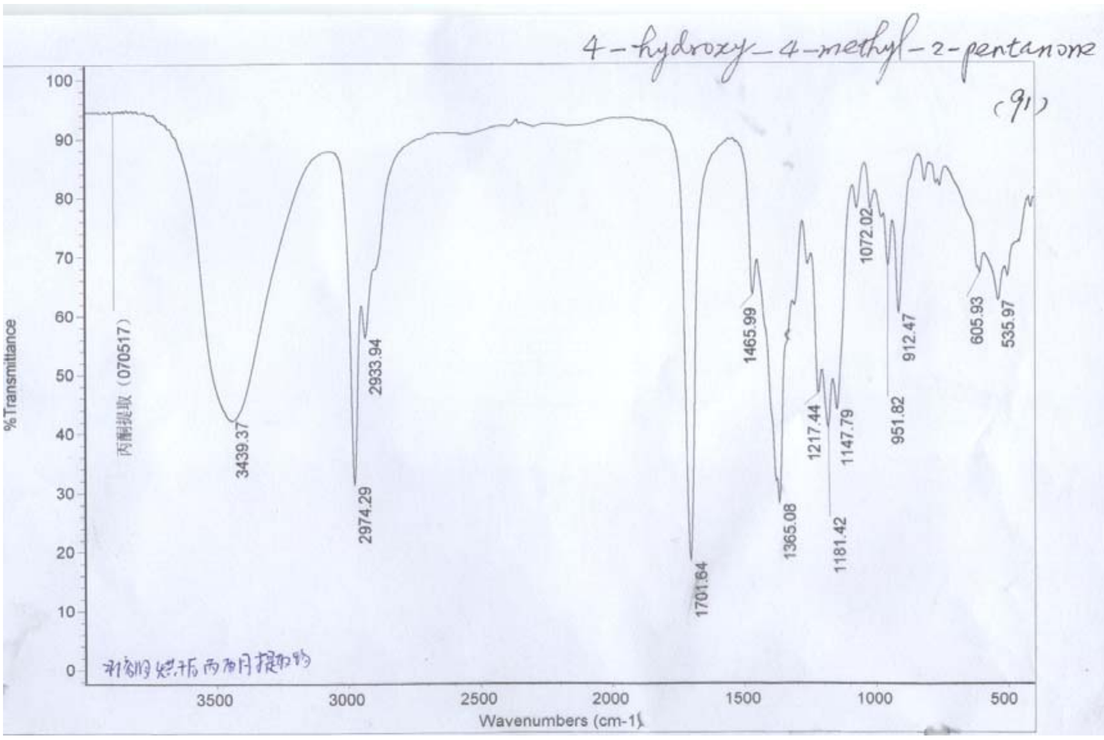


Fig. 10. The IR spectra of the solid composition in the displacement fluid

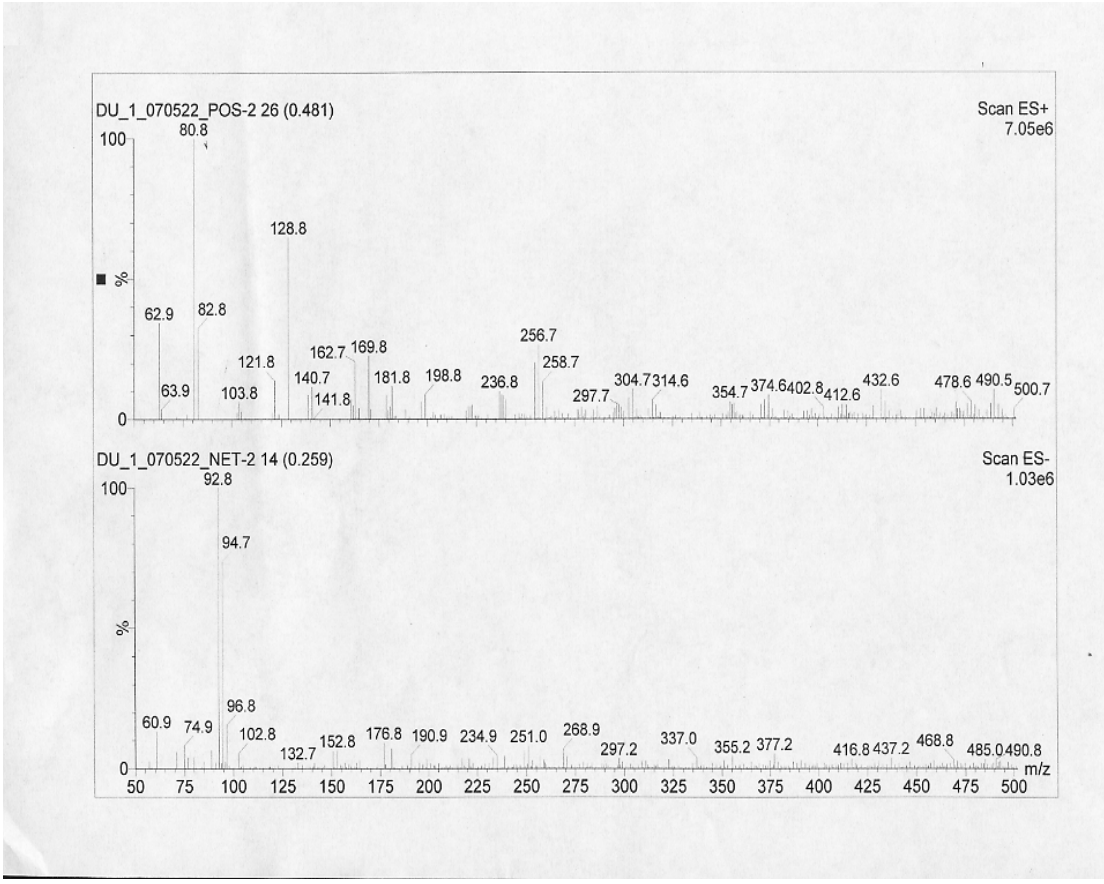


Fig 11. The mass spectrogram of the solid composition in the displacement fluid

3.5 Diffusion in the compound system

Several important factors affect the diffusion of the acdic-active substance in compound system. These include temperature,ionic strength and viscosity.The temperature is constant in these experiments, while the ionic strength is affected primarily by the sodium hydrate concentration. In 1960, R.B.Bird and his company had found the Stokes-Einstein equation[8] that express diffusion coefficient is related to solution viscosity as follows:

$$D = kT/6\pi\mu_n r \qquad [1]$$

where the $\boldsymbol{\mu_n}$ is the viscosity of the medium, ***D*** is the diffusion coefficient, and ***r*** is the radius of the molecule. The temperature and the viscosity are costant, so ***D*** is costant too. According to Van hunsel and Joos.[9]

$$IFT(t) = IFT_e + \frac{RT\Gamma^2}{C_o}(\pi/4Dt)^{1/2} \qquad [2]$$

where IFT(t) is interfacial tension as a function of time, t, IFTe is the equilibrium IFT, Co is the initial

[8] P. B. Bird, W. E. Stewart and E. M. Lightfoot. *Transport Phenomena*. New York: Wiley, Chapter 19,1960.
[9] J. van Hunsel and P. Joos, (1989). Colloid Polym. *Sci*, 2671026

surfactant concentration, and ***Γ*** is the adsorption at the interface. For compound system, *Co* and ***Γ*** will vary with alkali concentration, among other things[10]. If IFT is plotted versus $t^{-1/2}$, a straight line signifies that the process is diffusion controlled.

Table 2 summarizes the slope (inversely proportional to $D^{-1/2}$) and the intercept obtained in each case,where IFT is plotted before and after the minimum IFT is reached. Fig 12 shows the linear relationship between IFT and $t^{-1/2}$ at a sodium chloride of 1.5mass%, an alkali concentration of 0.3mass% and a surfactant concentration of 0.2mass%. It can clearly be seen that the slope of the line increases, the intercept of the line decrease and regression data R^2 decrease too as the contact time (T') increase before the minimum IFT is reached. Fig 13 shows that after the minimum IFT is reached, the slope of the line decrease ,the intercept of the line increase and regression data R^2 decrease as the contact time (T') increase.

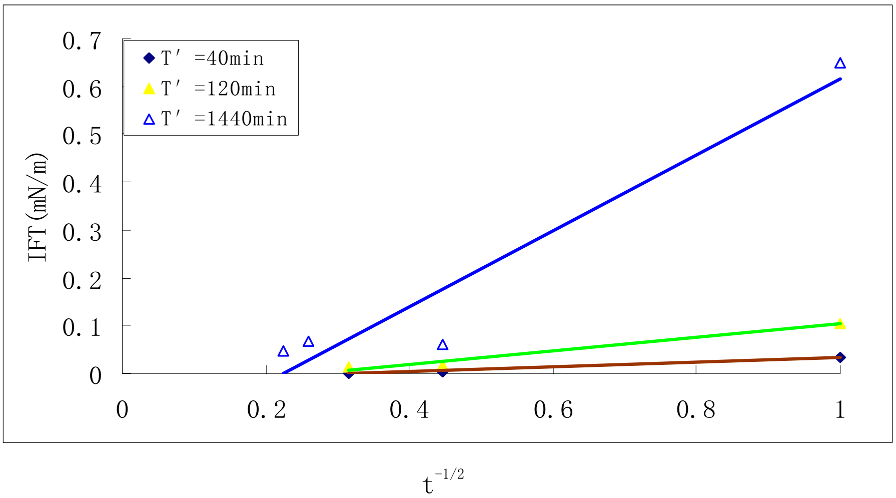


Fig. 12. IFT versus $t^{-1/2}$; effecet of contact time at compound system, approaching the minimum IFT

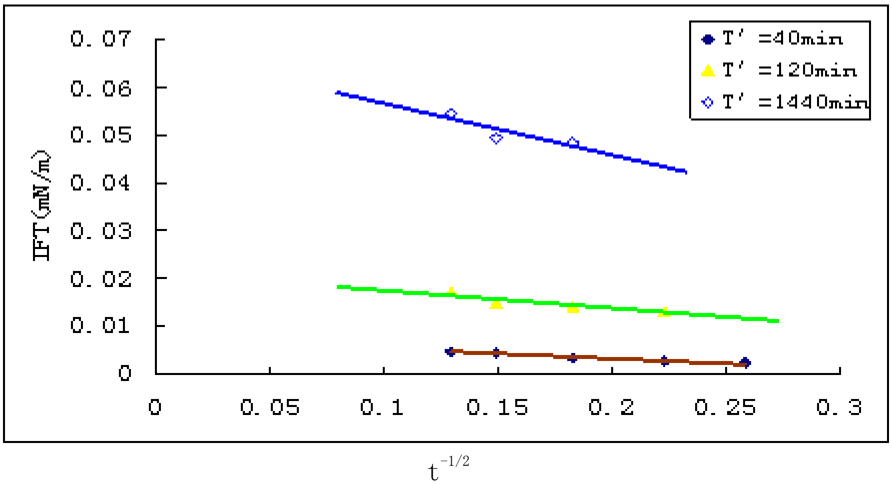


Fig. 13. IFT versus $t^{-1/2}$; effecet of contact time at compound system, after the minimum IFT

[10] Kevin C Taylor,Hisham A Nasr-EL-Din. (1996). The effect of synthetic surfactants on the interfacial behavior of crude oil/alkali/polymer systems,Colloids.and Surfaces A:Physicochemical and Engineering Aspects, 108（1）:49-72.

Table 2. Regression data, IFT versus $t^{-1/2}$

contact time, min	40min	120min	1440min
Slope1 ($Nm^{-1}min^{1/2}$)	0.0501	0.1416	0.7937
Intercept1(Nm^{-1})	-0.0161	-0.0384	-0.1763
R1(square)	0.9904	0.9798	0.9287
Slope2 ($Nm^{-1}min^{1/2}$)	-0.0203	-0.0375	-0.1061
Intercept2(Nm^{-1})	0.0073	0.0213	0.0671
R2(square)	0.9681	0.7867	0.7713

1- approaching the minimum; 2-after the minimum

Because IFT is plotted versus $t^{-1/2}$, a straight line signifies that the process is diffusion controlled. The acidic-active substance react with alkali first, and generate surfactant oil itself, then these surfactant adhere at the interface of the oil/ aqueous. They began to diffuse to the aqueous after achieve a maximum value. And the regression data R^2 decrease as the contact time increase, this phenomenon indicate that diffusion process diminish and not work at last. Finally the surfactant was even in the compound system.

4. CONCLUSION

1st. With the prolonging of the contact time, the IFT of the compound system increases fast, and the equilibrium value increases slowly. The ratio between them gradually enlarges and closes to 1 at last. And the line becomes more and more smooth. The reason for this phenomenon may lie in the consumption and diffusion of the acidic-active substance. In fact the formed interfacial film influences the arrangement of the surfactant. It is likely that these two factors interact together. In a word, the details need a further study.

2nd. Alkali can react with the active substance of the oil and generate surfactant in site. This surfactant could help the artificial surfactant adhere to the oil/ aqueous interface, further decrease the IFT. In the experiment, a little amount of alkali is required.

3rd. Before and after IFT minimum is reached, IFT is plotted versus $t^{-1/2}$, a straight line signifies that the process is diffusion controlled.

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