
14 Formation of Crude Oil Emulsions in Chemical Flooding

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CONTENTS

14.1	Introduction	518
14.2	Effect of Alkali	519
14.2.1	Experimental	519
14.2.1.1	Separation of Crude Oil Fractions	519
14.2.1.2	Elemental Composition and Molecular Weight	520
14.2.1.3	Model Emulsions and Measurement of Interfacial Properties	520
14.2.2	Results and Discussion	521
14.2.2.1	Physical Properties of Crude Fractions	521
14.2.2.2	Interfacial Tension	523
14.2.2.3	Interfacial Shear Viscosity	524
14.2.2.4	Zeta Potential	526
14.2.2.5	Stability of Emulsions	528
14.3	Effect of Hydrolyzed Polyacrylamide	534
14.3.1	Experimental	534
14.3.2	Results and Discussion	534
14.3.2.1	Interfacial Tension	534
14.3.2.2	Interfacial Shear Viscosity	534
14.3.2.3	Zeta Potential	535
14.3.2.4	Stability of O/W Emulsions	536
14.4	Effect of Surfactant	538
14.4.1	Experimental	538
14.4.2	Results and Discussion	538
14.4.2.1	Interfacial Tension	538
14.4.2.2	Interfacial Shear Viscosity	538
14.4.2.3	Zeta Potential	539
14.4.2.4	Stability of Emulsions	540
14.5	Effect of Alkaline–Surfactant–Polymer	542
14.5.1	Interfacial Tension	543
14.5.2	Interfacial Shear Viscosity	543
14.5.3	Zeta Potential	544
14.5.4	Stability of Emulsions	545
14.6	Conclusion	546
	Acknowledgments	546
	References	546

14.1 INTRODUCTION

Alkaline–surfactant–polymer (ASP) flooding is a new technique that has been tested in Da Qing and Sheng Li oil fields in China in the past few years. The technique uses partially hydrolyzed polyacrylamide (HPAM) as the polymer, petroleum sulfonate (ORS-41 or TRS) as the surfactant, and sodium hydroxide (NaOH) or sodium carbonate (Na_2CO_3) as the alkaline component. Compared with waterflood ASP flooding may increase oil recovery efficiency by about 15 to 20%, but the use of the new technique is faced with new problems. The production fluids form stable w/o and o/w emulsions and the separation of crude oil and water becomes more difficult. It is believed that the alkali, surfactant, and polymer used in the chemical flooding causes these problems [1].

The concentration of alkali used for ASP flooding is about 0.8 to 1.2% in water; the alkali reacts with the acidic components (resins and asphaltenes) in crude oil and form interfacially active components that accumulate at the oil–water interface and facilitates the formation of emulsion [1]. The stability of this emulsion depends on the concentration of the reservoir formed alkali–oil surfactant at the interface. This again depends on the concentration of the potential acidic components from crude oil that form interfacially active soap components [1]. However, Da Qing crude oil contains very little asphaltene (paraffinic crude oil), and has lower acid number, when sodium hydroxide used as the alkaline component in the recovery of crude was enhanced and the oil recovered also contained stable water-in-crude-oil emulsion. Some of the studies concerning the stability of water-in-crude-oil emulsions have shown that the surfactant and the polymer are not responsible for enhancing the stability of the water-in-oil emulsion [1]. HPAM enhances mainly the stability of oil-in-water emulsions and makes the water treatment difficult. Our investigations revealed that the resin, asphaltene, and saturated fractions of Da Qing crude oil reacted with sodium hydroxide and for a few days were unable to form stable emulsions. The anomalous behavior of the paraffinic crude oil in enhancing the stability of water-in-crude-oil emulsion in the presence of sodium hydroxide in the oil field led us to carry out a laboratory study regarding the chemical nature of the problem. To understand the formation of water-in-oil emulsions of Da Qing crude oil our focus is to study the long time effect of NaOH with the saturated fraction of the crude.

The concentration of the surfactant used for ASP flooding is about 0.1–0.3% in water. As an effect of surfactant coordinate with alkali the interfacial tension between crude oil and ASP solution may be decreased to 10^{-3} mNm^{-1} . Therefore, the crude and ASP solution can be emulsified in reservoir and pipelines during crude production.

The concentration of the polymer used for ASP flooding is 1000 to 2400 mg/l. After the polymer solution passes through the reservoir for months or years the concentration of the polymer in the production water is about 10 to 300 mg/l. It is believed that the polymer in the water is responsible for enhancing the stability of o/w emulsion [1]. The content of crude oil in the production water after treatment by present technology is about 2300 mg/l that is much higher than the standard value of 30 mg/l in Sheng Li oil field.

In a series of articles Sjöblom and co-workers have investigated the properties of water-in-crude-oil emulsions based on the North Sea crude oils [2–16]. Interests has focused on different aspects of stability, destabilization, and separation of interfacially active components, dielectric properties, and the design of adequate model systems. Furthermore, chemical modifications of the interfacially active components, both artificial and natural aging, have been carried out to understand the effect of molecular properties on the stability of water-in-crude-oil emulsions.

Crude oil is a mixture of aliphatic and aromatic hydrocarbons, and oxygen-, nitrogen-, and sulfur-containing compounds such as resins and asphaltenes. There is no doubt that the

interfacially active components come from resins and asphaltenes of the crude oils [17]. The asphaltene fraction from crude oils can be adsorbed on the interface between oil and water, and forms stable film to stabilizing crude emulsions [18]. Resins and asphaltenes are polymeric, containing polyaromatic structures, and possess structural similarities between them [17]. They are differentiated by their solubility in light hydrocarbons such as pentane. This differentiation itself clearly indicates that the resins (soluble in pentane) are smaller on a molecular level compared to asphaltenes (insoluble in pentane). Within each fraction of resins and asphaltenes, there is a range of components that are of different sizes and contain different functional groups. The molecules of asphaltenes contain condensed aromatic rings of different sizes. The asphaltenes contain large condensed aromatic rings compared to resins [2]. The stability of water-in-crude-oil emulsions depends on the total structure of the molecular matrix of the interfacially active components. Size, aromaticity, types of carbonyl functionality, and other functional groups in the bulk play an important role in the total stability of the emulsions.

All these studies have given us insight into the problems relating to stability of water-in-crude-oil emulsions. It is obvious that a study that aims to understand the problems related in the ASP flooding technique should involve the interfacially active components from the crude oil. However, the effect of alkali, surfactant, and polymer reactions with the interfacially active fractions from crude oil on the stability of emulsions has not been fully studied.

In order to study the formation of crude oil emulsions in ASP flooding and the effect of alkali, surfactant, and polymer reactions with the interfacially active fractions from crude oil on the stability of emulsions, the saturated, aromatic, resin, and asphaltene fractions from a crude oil in Da Qing oil field and two Gu Dong crude oils from Sheng Li oil field in China were separated first. Then the acid number, elemental composition, and molecular weight determinations of the fractions were made to evaluate the properties of the fractions. The correlations between the physical properties and molecular parameters such as molecular weight and functional groups were explored. Furthermore, the fractions were then used to prepare model oils with additive-free jet oil. The interfacial tension, interfacial shear viscosity, and zeta potential between the model oils and ASP solution and the stability of the emulsions formed with the model oils and ASP solution were determined.

14.2 EFFECT OF ALKALI

In this study the alkali solution used for Gu Dong model oils is 1.2% Na_2CO_3 solution and for Da Qing model oils is 1.2% NaOH solution. The alkali solution was prepared with double-distilled water.

14.2.1 EXPERIMENTAL

14.2.1.1 Separation of Crude Oil Fractions

The interfacially active fractions of saturated, aromatic, resin, and asphaltene used in these experiments were separated from Da Qing and Gu Dong crude oils. The separation of asphaltene fractions from the crude oil was carried out by pentane precipitation. One hundred grams of crude oil was agitated with 3000 ml of pentane at room temperature for 30 min. The mixture was then left to stand for 15 days. The precipitated asphaltene fraction was filtered and washed with a small portion of pentane and dried. The filtrate from the above was then poured on a column containing Al_2O_3 . The saturate fraction was extracted by 8000 ml petroleum ether, the aromatic fraction was extracted by 8000 ml benzene, the resin 1 fraction was extracted by

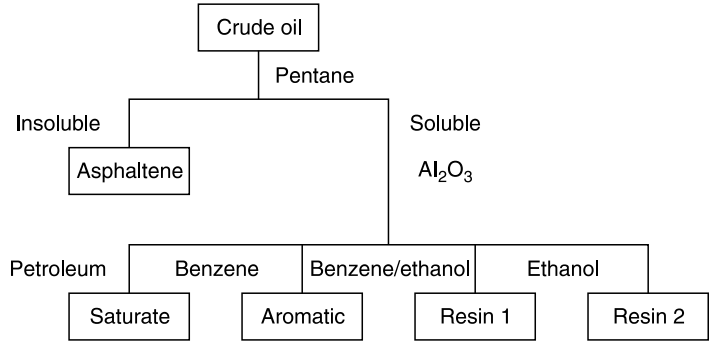


FIGURE 14.1 Separation of crude oil fractions.

TABLE 14.1
Composition of Model Oil (wt%)

	Crude Oil	Saturate	Aromatic	Resin 1	Asphaltene
Gu Dong 1 [#]	10.00	4.59	2.25	1.49	1.44
Gu Dong 4 [#]	10.00	4.02	2.19	1.49	1.14
Da Qing	10.00	6.43	1.52	1.41	0.10

4000 ml benzene/ethanol (benzene/ethanol ratio: 1/1, v/v), and the resin 2 fraction was extracted by 4000 ml ethanol. The separation scheme is presented in Figure 14.1.

14.2.1.2 Elemental Composition and Molecular Weight

The relative molecular weight of the fractions was measured by the VPO method using a molecular weight meter (Knauer, Germany). The elemental composition of the crude oil was determined by Elementar Analysen Systeme, Vario El, Germany.

14.2.1.3 Model Emulsions and Measurement of Interfacial Properties

The water used in the experiments was double-distilled water or alkaline, surfactant, polymer solution. A jet fuel from a refinery without any additives was used as the dispersion media of the model oils. The jet fuel was purified by silica adsorption before the experiments were carried out. The composition of the model oils is shown in Table 14.1. The weight percentage of each fraction is selected to represent the weight percentage of the fraction (around 10%) in the crude oils (Table 14.2). This would allow us to compare the stability of emulsions formed between model oils containing the fractions and the chemical solutions. From Table 14.1 the crude model oil contains 10% of the crude oils in the jet oil and the saturate model oil contains 4.59%, 4.02%, and 6.43% saturated fraction from Gu Dong 1[#], Gu Dong 4[#], and Da Qing crude oils, respectively.

The model emulsions were prepared by mixing the model oils and alkaline solution (o/w ratio: 2/8, v/v) in a 50 ml cylinder. The emulsification was carried out by shaking the cylinder 50 times at 60 °C. The emulsification was done twice every day and the stability of the emulsions

TABLE 14.2
Composition of Crude Oil Fractions

Fraction	Wt %		
	Gu Dong 1 [#]	Gu Dong 4 [#]	Da Qing
Saturate	47.08	46.54	68.09
Aromatic	23.65	28.18	17.25
Resin 1	14.73	13.81	14.47
Resin 2	0.11	0.12	0.10
Asphaltene	14.43	11.35	0.09

was determined visually by measuring the water separated from the emulsions at 60 °C as a function of time. The emulsion stability experiments were carried out for 84 days. This would allow us to investigate the effect of reaction time of the alkali on the properties of the model emulsions.

The interfacial tension between the model oils and distilled water or the chemical solution was measured by a spinning drop interfacial tension meter (JJ2000A, Shanghai, China) at 45 °C. The interfacial shear viscosities were measured using a SVR-S Interfacial Viscoelastic Meter (Kyowa Kagaku Co. Ltd, Japan) [18] at 25 °C.

The zeta potential on oil droplets was measured by a zeta potential meter (ZPOM, Kyowa Kagaku Co. Ltd, Japan) at 25 °C. There was about 10 mg/l oil in the emulsion (o/w) used for zeta potential measurement.

14.2.2 RESULTS AND DISCUSSION

14.2.2.1 Physical Properties of Crude Fractions

The composition of the crude oils is given in Table 14.2; the content of asphaltene fraction in Gu Dong 1[#] and Gu Dong 4[#] crude oils is 14.43% and 11.35% but it is only 0.09% in Da Qing crude oil. Da Qing crude contains more saturate fraction than Gu Dong crude oils. Because the resin 2 fraction is too little to do experiments in the work resin 1 fraction is presented as the resin fraction in this chapter.

The elemental composition of the crude oils and their fractions is given in Table 14.3. The value of the H:C ratio decreased in the order of saturated > aromatic ≈ resin > asphaltene for the three crude oils.

Table 14.4 shows that the saturate fraction from Da Qing crude oil contains most oxygen (0.375 g in 100 g crude oil), following with the asphaltene fractions from Gu Dong 1[#] and Gu Dong 4[#] crude oils. The asphaltene fraction from Da Qing crude oil contains only 0.001 g oxygen in 100 g crude oil.

The molecular weight and acid number of the fractions are given in Tables 14.5 and 14.6. It is clear that the molecular weight of the fractions is in the order of saturated < aromatic < resin < asphaltene for all of the three crude oils and the molecular weight of the crude oils is close to their saturated fraction, respectively.

The values presented in Table 14.6 clearly shows that the acid number of the fractions is in the order of saturated < aromatic < resin < asphaltene for Gu Dong crude oils. The order is the same as the order of molecular weight of the fractions. The acid number of the fractions from

TABLE 14.3
Elemental Composition of Crude Oils and their Fractions

Crude oil	Fraction	w(C)/%	w(H)/%	w(O)/%	w(S)/%	w(N)/%	n(H):n(C)
Gu Dong 1 [#]	Saturate	86.37	13.24	0.25	0.65	1.00	1.84
	Aromatic	87.76	10.38	0.72	0.69	1.20	1.42
	Resin 1	85.06	10.12	1.32	0.72	1.47	1.43
	Asphaltene	85.97	9.38	2.19	0.50	1.47	1.31
	Crude oil	86.70	11.71	0.79	0.38	1.01	1.62
Gu Dong 4 [#]	Saturate	86.12	13.16	0.30	0.59	0.89	1.83
	Aromatic	84.32	10.11	0.75	3.13	1.42	1.44
	Resin 1	84.08	10.31	1.91	2.18	1.48	1.47
	Asphaltene	81.67	8.89	2.79	4.63	1.44	1.31
	Crude oil	84.88	11.35	0.86	0.41	1.10	1.60
Da Qing	Saturate	85.54	14.26	0.55	0.03	0.73	1.96
	Aromatic	86.92	11.22	0.50	0.34	1.53	1.52
	Resin 1	86.25	10.79	1.48	0.45	1.03	1.50
	Asphaltene	86.19	10.53	1.14	0.18	1.09	1.47
	Crude oil	86.53	12.50	0.73	0.13	0.86	1.73

TABLE 14.4
Oxygen in Crude Oil Fractions

Fraction	Oxygen in 100 g Crude Oil/g		
	Gu Dong 1 [#]	Gu Dong 4 [#]	Da Qing
Saturate	0.118	0.140	0.375
Aromatic	0.170	0.211	0.086
Resin 1	0.194	0.264	0.214
Asphaltene	0.316	0.317	0.001

TABLE 14.5
Molecular Weights of Crude Oils and their Fractions

Crude Oil	Saturate	Aromatic	Resin 1	Asphaltene	Crude Oil
Gu Dong 1 [#]	434	601	1025	1499	433
Gu Dong 4 [#]	503	728	1117	1308	427
Da Qing	485	773	1396	2433	480

Da Qing crude oil is in the order of saturated < aromatic < asphaltene < resin. It seems that the resin fraction contains more acidic matters than the asphaltene fraction in Da Qing crude oil.

The above facts indicate that the asphaltene molecules are large, polyaromatic, and contain the highest acidic oxygen components among the fractions for Gu Dong crude oils, and the resin fraction from Da Qing crude oil contains the highest acidic oxygen components among the fractions from the crude oil.

TABLE 14.6
Acid Numbers of Crude Oils and their Fractions

Fraction	Gu Dong 1 [#]	Gu Dong 4 [#]	Da Qing
Saturate	2.397	3.014	0.4760
Aromatic	5.386	5.242	1.039
Resin 1	6.001	8.002	5.101
Asphaltene	16.45	8.378	4.213
Crude oil	3.640	3.217	0.5174

TABLE 14.7
Interfacial Tension Between Model Oils and Aqueous Phases (45 °C)

Crude Oil		Model Oil				
		Saturate	Aromatic	Resin 1	Asphaltene	Crude oil
Gu Dong 1 [#]	w %	4.60	2.53	1.46	1.44	10.00
	$\gamma_{o/w}/\text{mN m}^{-1}$	35.70	24.52	22.76	19.38	11.89
	$\gamma_{o/s}/\text{mN m}^{-1}$	13.36	5.61	4.63	0.056	0.93
	w %	3.00	3.00	3.00	3.00	3.00
	$\gamma_{o/w}/\text{mN m}^{-1}$	33.03	17.90	15.78	12.75	19.27
	$\gamma_{o/s}/\text{mN m}^{-1}$	11.22	4.37	3.12	0.0053	0.762
Gu Dong 4 [#]	w %	4.02	2.19	1.38	1.14	10.00
	$\gamma_{o/w}/\text{mN m}^{-1}$	33.55	18.85	18.36	16.90	17.21
	$\gamma_{o/s}/\text{mN m}^{-1}$	9.12	7.11	4.30	0.86	1.71
	w %	3.00	3.00	3.00	3.00	3.00
	$\gamma_{o/w}/\text{mN m}^{-1}$	30.07	14.42	13.33	7.03	21.48
	$\gamma_{o/s}/\text{mN m}^{-1}$	10.45	5.32	2.62	0.43	1.35
Da Qing	w %	6.66	1.58	1.45	0.10	10.00
	$\gamma_{o/w}/\text{mN m}^{-1}$	39.96	33.57	27.63	33.68	30.46
	$\gamma_{o/s}/\text{mN m}^{-1}$	18.31	11.97	8.24	12.81	4.04
	w %	3.00	3.00	3.00	3.00	3.00
	$\gamma_{o/w}/\text{mN m}^{-1}$	36.51	30.24	26.34	28.22	29.40
	$\gamma_{o/s}/\text{mN m}^{-1}$	14.68	10.30	2.64	4.07	2.86

14.2.2.2 Interfacial Tension

The interfacial tension between the model oils and aqueous phases is shown in Table 14.7.

It shows that the interfacial tension between the model oils and alkali solutions ($\gamma_{o/s}$) is lower than the interfacial tension between the same model oil and distilled water ($\gamma_{o/w}$).

This indicates that all the fractions from the crude oils which reacted with the alkali are able to form interfacially active components, and these components are more interfacially active than the indigenous interfacially active components in the crude oil. Therefore, the interfacial tension was decreased.

It is interesting to note that the interfacial tension between the asphaltene model oils and Na_2CO_3 solution is lower than the interfacial tension between the crude model oils and the alkaline solution for Gu Dong 1[#] and Gu Dong 4[#] crude oils, especially the very low interfacial tension between asphaltene model oil and Na_2CO_3 solution for Gu Dong 1[#] crude oil (0.056 to 0.0053 mN m^{-1}). It appears that the formation of interfacially active components is very significant in the reaction of the alkaline and asphaltene fraction. It is clear that the asphaltene fraction dominates the interfacial tension between crude model oil and the alkali solution comparing the interfacial tension between other fraction model oils and alkali solution for Gu Dong crude oils. For Da Qing crude oil a resin fraction dominates the interfacial tension between crude model oil and NaOH solution. From Tables 14.4 and 14.6 it is clear that the asphaltene fraction of Gu Dong crude oils contains more oxygen and has a higher acid number, and the resin fraction of Da Qing crude oil contains more oxygen and has a higher acid number, compared with other fractions. It seems that the interfacially active components formed in the reaction of the alkali and the acidic oxygen components in asphaltene or resin fractions contribute to decrease the interfacial tension.

14.2.2.3 Interfacial Shear Viscosity

Figures 14.2 to 14.4 show that the interfacial shear viscosity between asphaltene or resin model oil and alkali solution is higher than the interfacial shear viscosity between the model oils and distilled water. It is clear that the interfacially active components formed in the reaction of the alkali and asphaltene or resin fraction are accumulated at the interface and the interfacial film has higher mechanical strength [19].

Figures 14.5 to 14.7 show that the interfacial shear viscosity between asphaltene model oils and Na_2CO_3 or NaOH solution has the highest value among the model oils and the alkali solutions measured. These indicate that the interfacial film of the interfacially active components formed in the reaction of asphaltene fractions and alkali solutions has the highest mechanical strength and is able to enhance the stability of w/o emulsions. Because the asphaltene fraction has the largest molecular weight it is obvious that the interfacially active components formed in the reaction

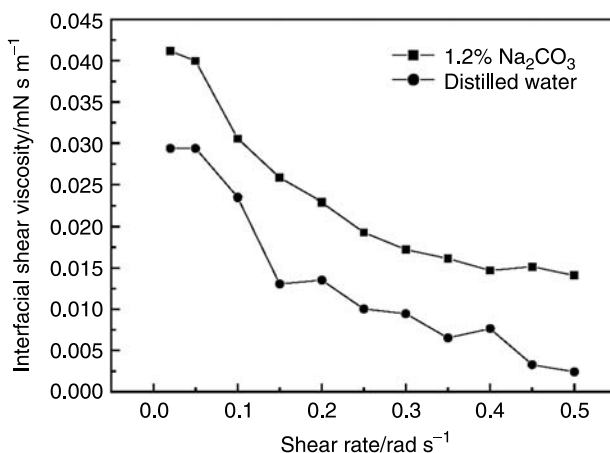


FIGURE 14.2 Interfacial shear viscosity between 2% asphaltene model oil (Gu Dong 1[#]) and distilled water/1.2% Na_2CO_3 solution, 25 °C.

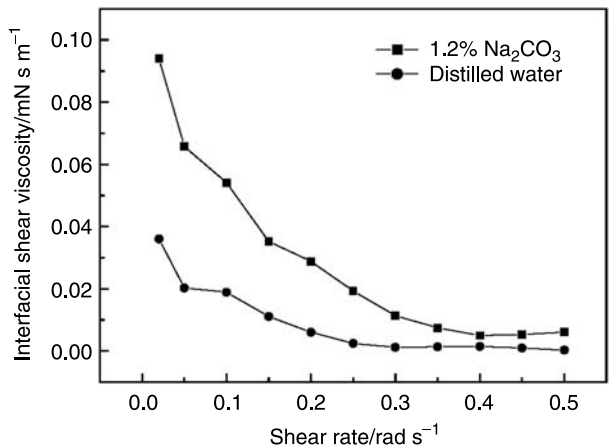


FIGURE 14.3 Interfacial shear viscosity between 2% asphaltene model oil (Gu Dong 4[#]) and distilled water/1.2% Na₂CO₃ solution, 25 °C.

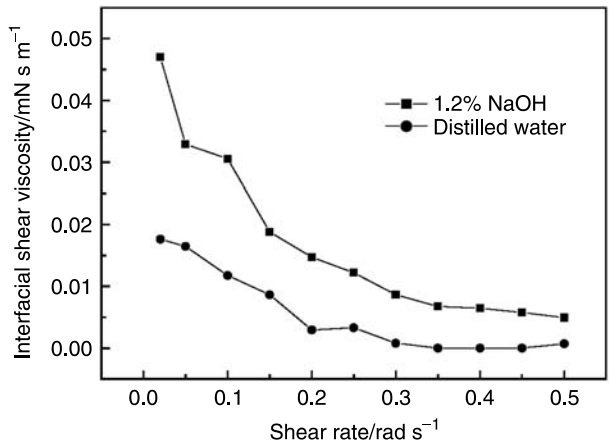


FIGURE 14.4 Interfacial shear viscosity between 2% resin model oil (Da Qing) and distilled water/1.2% NaOH solution, 25 °C.

have a larger molecular weight than that formed in the reaction of the alkali with other fractions. This proves that the interfacially active component which has a larger molecular weight is able to form more stable interfacial film and emulsions. It should also be noted that the interfacial shear viscosity of the film is decreased as the shear rate increases. This phenomenon shows that the film was structured and the structure was broken down as the shear stress was increased.

Figures 14.8 to 14.10 show that the interfacial shear viscosity between the model oils prepared with deasphalted crude oil and alkali solutions is lower than that of crude model oil and the alkali solutions, and the interfacial shear viscosity increases with the concentration of the crude oils in the jet fuel oil. This is a further indication that the asphaltene fraction contributes to the formation of interfacially active components and enhanced the strength of the film.

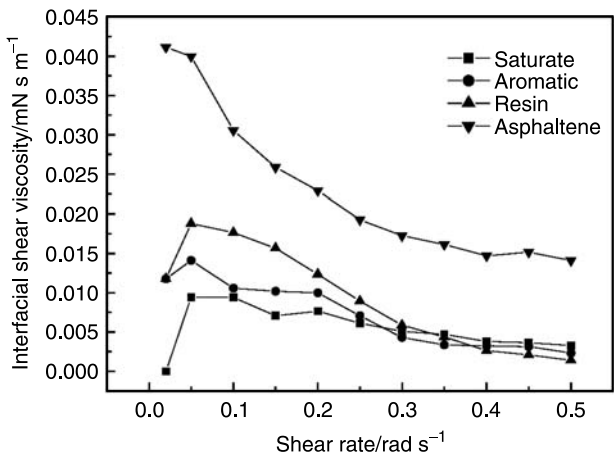


FIGURE 14.5 Interfacial shear viscosity between model oils (Gu Dong 1[#]) and 1.2% Na₂CO₃ solution, 25 °C.

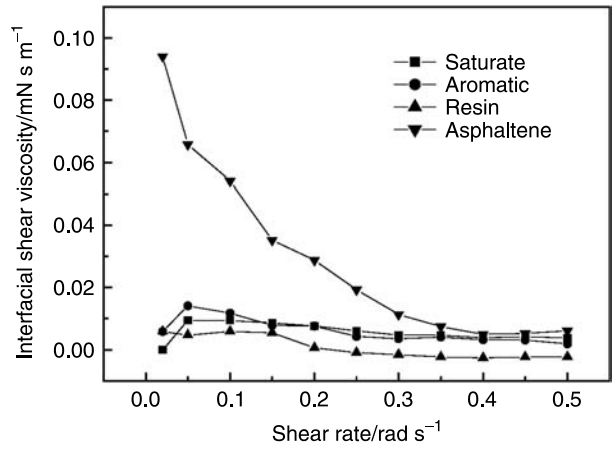


FIGURE 14.6 Interfacial shear viscosity between model oils (Gu Dong 4[#]) and 1.2% Na₂CO₃ solution, 25 °C.

All these experimental results proved that the interfacial film of the interfacially active components formed in the reaction of asphaltene fractions and alkali solutions has the highest mechanical strength and asphaltene fraction dominates the property of the interfacial film when the alkali solution was as aqueous phase.

14.2.2.4 Zeta Potential

Table 14.8 shows that the absolute value of zeta potential on the asphaltene model oil (Gu Dong 4[#] crude oil) droplets was increased with increase of the reaction time of asphaltene and Na₂CO₃. This shows that the interfacially active components formed in the reaction can

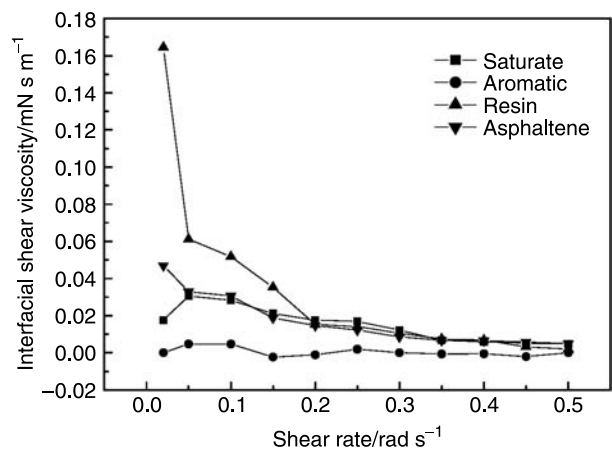


FIGURE 14.7 Interfacial shear viscosity between model oils (Da Qing) and 1.2% NaOH solution, 25 °C.

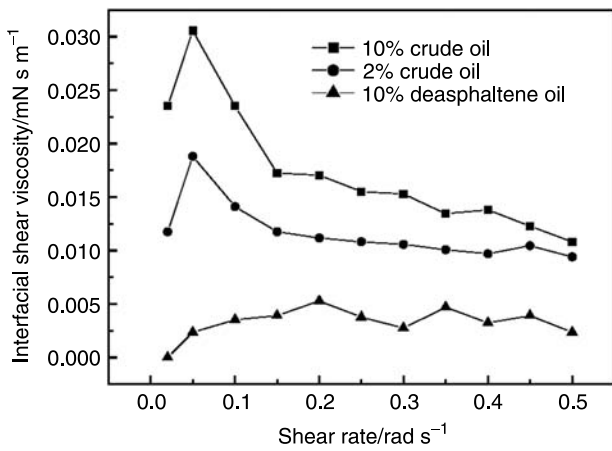


FIGURE 14.8 Interfacial shear viscosity between crude model oils (Gu Dong 1[#]) and 1.2% Na₂CO₃ water solution, 25 °C.

TABLE 14.8	
Influence of Reaction Time of Na ₂ CO ₃ Solution and 3% Crude Model Oil on Zeta Potential (mV, 25 °C)	
Reaction Time (days)	Zeta Potential (mV)
0	-27.3
1	-45.9
10	-47.5

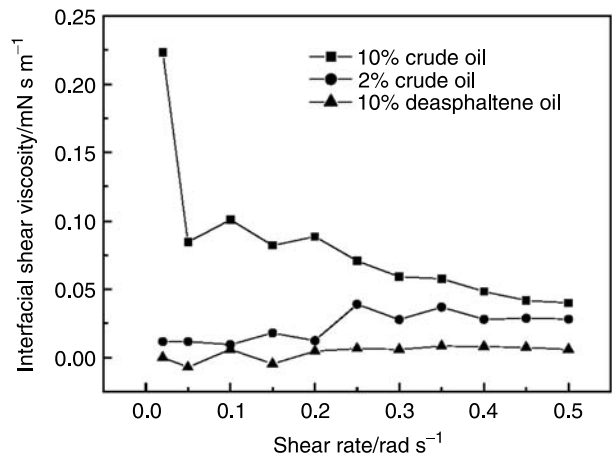


FIGURE 14.9 Interfacial shear viscosity between crude model oils (Gu Dong 4[#]) and 1.2% Na₂CO₃ water solution, 25 °C.

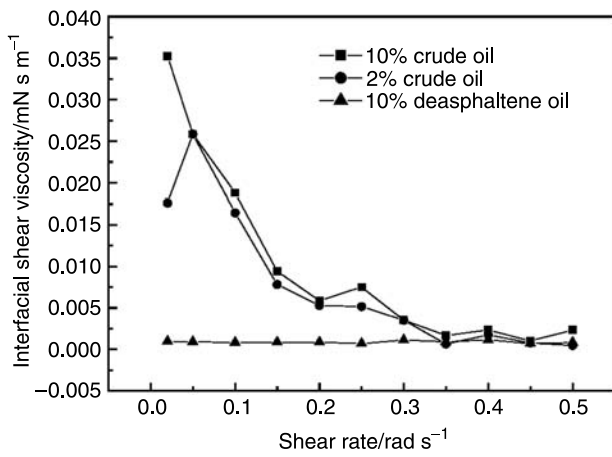


FIGURE 14.10 Interfacial shear viscosity between crude model oils (Da Qing) and 1.2% NaOH water solution, 25 °C.

also change the electrical property of the interfacial film between the oil and water phase, and the effect is more significant as the reaction time is increased. Therefore, the interfacially active components are able to enhance o/w emulsion stability.

14.2.2.5 Stability of Emulsions

The stability of asphaltene model oil emulsions and crude model oil emulsions of Gu Dong 1[#] crude oil are presented in [Figures 14.11](#) and [14.12](#). When distilled water was the aqueous phase both the asphaltene model oil and the crude model oil were unable to form stable emulsions as the oils and the water reacted in 54 days. When 1.2% Na₂CO₃ solution was the aqueous phase no water separated from the asphaltene model oil emulsions and crude model oil emulsions after

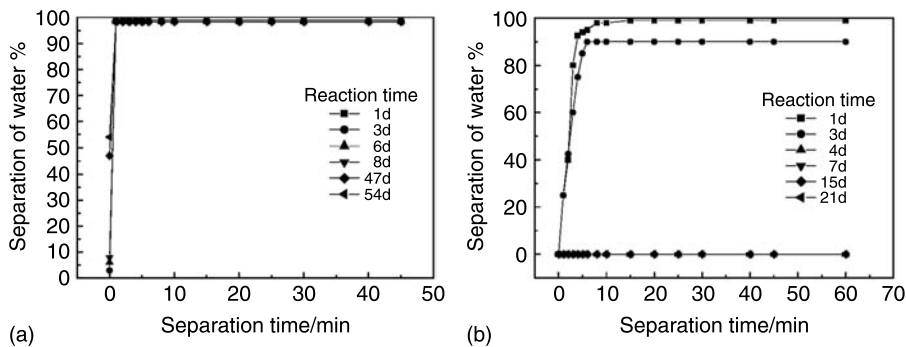


FIGURE 14.11 Stability of the emulsion formed of asphaltene model oil (Gu Dong 1[#]) and distilled water (a) or 1.2% Na₂CO₃ water solution (b), 60 °C.

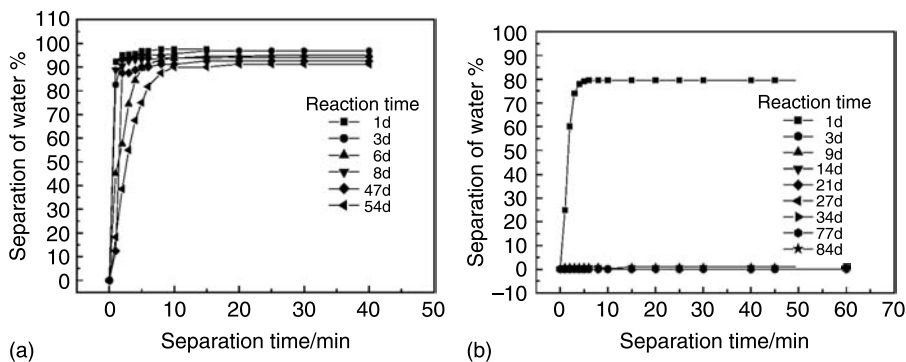


FIGURE 14.12 Stability of the emulsion formed of crude model oil (Gu Dong 1[#]) and distilled water (a) or 1.2% Na₂CO₃ water solution (b), 60 °C.

a period of 7 or 3 days' reaction of the oil and water. In contrast, the saturated, aromatic, and resin model oils tested in the same manner were not able to form stable emulsions even after 2 months of reaction. It is clear that the asphaltene fraction is responsible for stabilizing Gu Dong 1[#] crude oil emulsions when Na₂CO₃ was used. This result is supported well by measurement of the interfacial shear viscosity of asphaltene model oil and the alkaline solution discussed above. This result also shows that the reaction of asphaltene and Na₂CO₃ may progress slowly until all the possible acidic oxygen is replaced by sodium atoms.

Figures 14.13 and 14.14 show a similar result to that in Figures 14.11 and 14.12. Also, the asphaltene fraction dominates the stability of Gu Dong 4[#] crude oil emulsions in the same manner as Gu Dong 1[#] crude oil emulsions. The difference between Gu Dong 1[#] and 4[#] crude oils is that the asphaltene and crude model oil emulsions of Gu Dong 4[#] crude oil are more stable than the emulsion of Gu Dong 1[#] crude oil when distilled water was as the aqueous phase.

Comparing the interfacial tension, interfacial shear viscosity, and the physical properties of the fractions from Gu Dong crude oils the study shows clearly that the asphaltene fractions from Gu Dong crude oils have more polar, larger, acidic components than the other fractions. The characteristics can also be generalized to asphaltene from other crude oils. The components

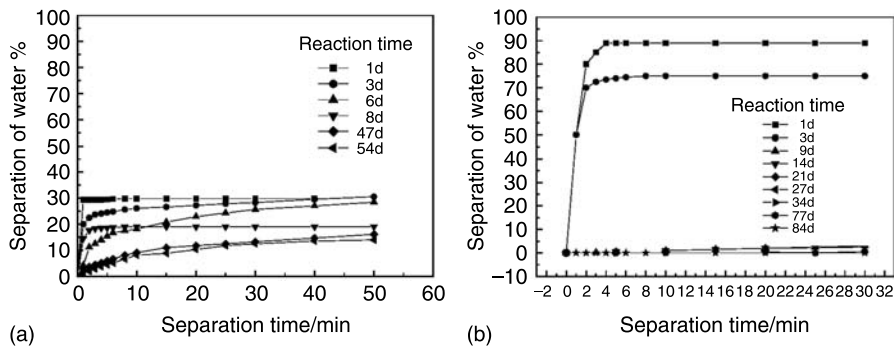


FIGURE 14.13 Stability of the emulsion formed of asphaltene model oil (Gu Dong 4[#]) and distilled water (a) or 1.2% Na₂CO₃ water solution (b), 60 °C.

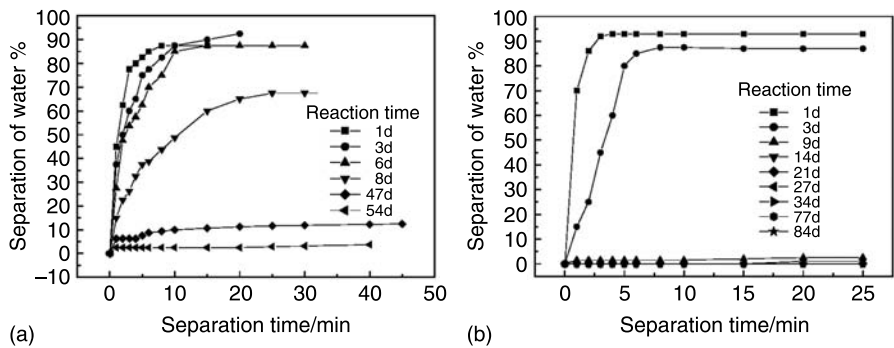


FIGURE 14.14 Stability of the emulsion formed of crude model oil (Gu Dong 4[#]) and distilled water (a) or 1.2% Na₂CO₃ water solution (b), 60 °C.

in the asphaltene fraction react with Na₂CO₃ solution and form soap-like interfacially active components which accumulate at the oil/water interface and form a rigid film around water droplets. Therefore, the film is able to prevent the coalescence of the droplets. The result also shows that the mechanical strength of the interfacial film can increase with the residence time of the sodium carbonate solution in the reservoir.

Compared with the emulsions of Gu Dong crude oil, the emulsions of Da Qing crude oil have different characteristics. Figures 14.15 and 14.16 show that the saturated and resin fractions reacted with NaOH are able to form more stable emulsions than the asphaltene fraction from Da Qing crude oil. The saturated and resin fractions help to stabilize the crude oil emulsion after reaction with NaOH. Like asphaltene model oil the aromatic model oils tested in the same manner were not able to form stable emulsions after 84 days of reaction with NaOH.

As with the asphaltene fraction from Gu Dong crude oils it is easy to understand why the resin fraction from Da Qing crude oil, when reacted with NaOH, can stabilize crude oil emulsion. The resin fraction has the highest acid number (5.101 in Table 14.6) among the fractions from Da Qing crude oil, and the interfacial tension between resin model oil and NaOH solution has the lowest value (2.64 mN m⁻¹ in Table 14.7). It is clear that the interfacially active components

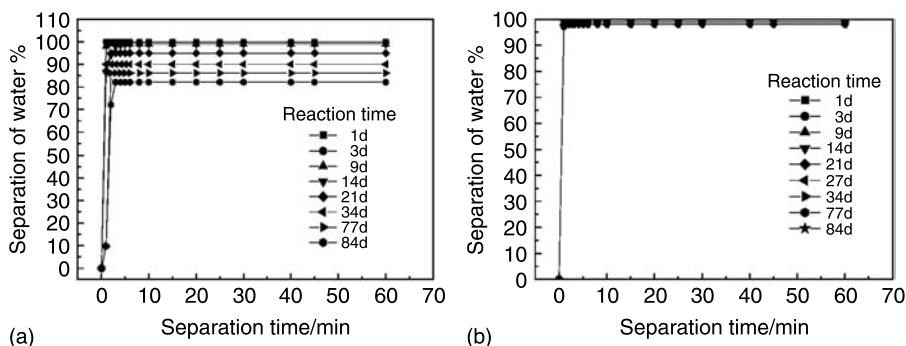


FIGURE 14.15 Stability of the emulsion formed with saturate model oil (a) or asphaltene model oil (b) (Da Qing) and 1.2% NaOH water solution, 60 °C.

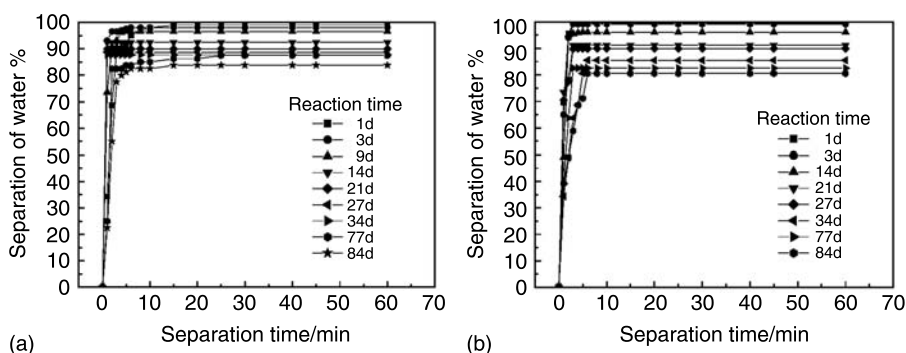


FIGURE 14.16 Stability of the emulsion formed with resin model oil (a) or crude model oil (b) (Da Qing) and 1.2% NaOH water solution, 60 °C.

were formed by the acidic components in the resin fraction reacted with NaOH. However, what are the components in the saturated fraction reacted with NaOH, and how is the emulsion stabilized? As a paraffinic crude oil Da Qing crude oil contains large saturate fraction (68.09%, Table 14.2). The saturate fraction contains the highest amount of oxygen (0.375 g; see Table 14.4) in 100 g crude oil and the lowest acid number (0.476; see Table 14.6). The interfacial tension between the saturated model oil of Da Qing crude oil and NaOH solution is the highest (14.68 to 18.31 mN m⁻¹; see Table 14.7). It is obvious that not only the acidic components but also some other substances in the saturated fraction reacted with NaOH and the components formed in the reaction are less interfacially active than the components formed in the reaction of resin fraction and NaOH.

To study the properties of the components formed in the reaction of saturate and NaOH the interfacial tension, interfacial shear viscosity during the reaction process, and infrared spectra of saturated fraction and the components formed were measured. The interfacial tension between saturated model oil and NaOH solution changed with reaction time is shown in Figure 14.17. The figure shows that interfacial tension decreased from the first day of the reaction. The interfacial tension decreased rapidly in the first week and slowly during the following 8 weeks.

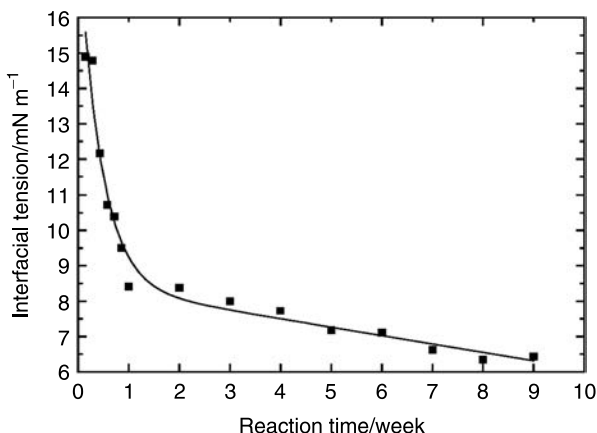


FIGURE 14.17 Interfacial tension changed with reaction time (5.0% saturate model oil, 0.6% NaOH solution, 30 °C).

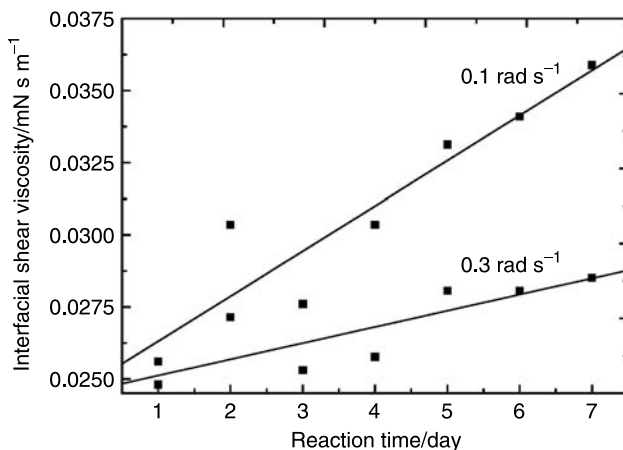


FIGURE 14.18 Interfacial shear viscosity changed with reaction time (3.0% saturate model oil, 0.6% NaOH solution, 25 °C).

The change of interfacial shear viscosity between the saturate model oil and NaOH solution during the first week is shown in Figure 14.18. An increase of the interfacial shear viscosity with reaction time confirms the formation of the interfacially active components again. Furthermore, the interfacial shear viscosity between the model oil and NaOH solution decreased and the increase of shear rate indicated that the interfacially active components form a network at the interface. This proves that the interfacial film formed by the interfacially active components has some strength and is able to stabilize emulsions.

IR spectroscopy (Figure 14.19(b)) shows absorption at 1563 cm^{-1} , which indicates the presence of COO^- groups in the component, and the absorption at 1100 cm^{-1} is due to the C–O stretching vibration of the carboxylic groups. This shows that sodium salts or soaps were formed

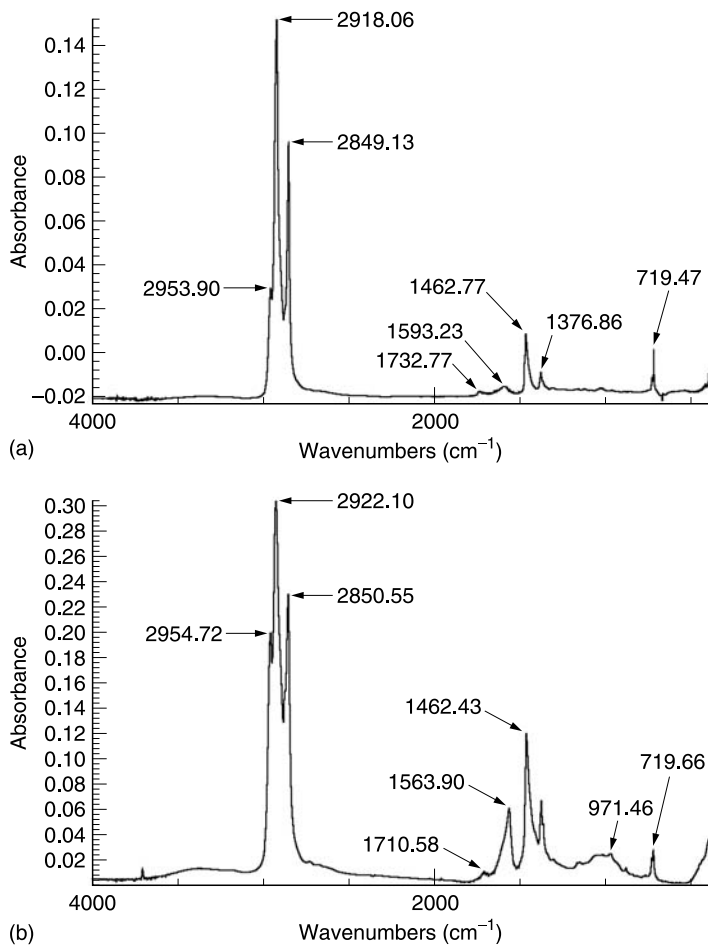


FIGURE 14.19 IR spectroscopy of saturate fraction (a) and the interfacially active components (b) formed in the reaction of saturate and NaOH.

in the reaction of the saturated fraction and NaOH. These salts or soaps may be formed by the reaction of NaOH with the acidic components and ester in the saturate fraction. Because the salts or soaps formed in the reaction have long hydrocarbon chains they are more oil soluble and less interfacially active than the components formed in the reaction of the resin fraction and NaOH.

The study above shows that the ASP flooding process in the reservoir provides sufficient time for the formation of interfacially active components, such as salt or soap, by the reaction of alkali with the acidic or nonacidic components in asphaltene, resin, and saturated fractions. These interfacially active molecules are responsible for providing stability for the water-in-crude-oil emulsion.

It is interesting that by using sodium carbonate solution as the alkaline component in the ASP technique for high acid number Gu Dong crude oils the reaction between the asphaltene fractions and alkali leads to stable emulsions. When sodium hydroxide is used as the alkaline

component for paraffinic Da Qing crude oil it is the saturated and resin fractions that lead to stable emulsions.

14.3 EFFECT OF HYDROLYZED POLYACRYLAMIDE

14.3.1 EXPERIMENTAL

The interfacially active fractions of asphaltene and resin fractions used in these experiments were separated from Gu Dong 4[#] crude oil. The resin and asphaltene model oils were prepared with jet fuel; the crude model oil is a mixture of 10% of the crude and 90% jet fuel. The aqueous phase used in the experiments was synthetic formation water (Table 14.9) or hydrolyzed polyacrylamide (HPAM) solution of the water. The polymer used was partially hydrolyzed polyacrylamide (HPAM, 3530S, France). The molecular weight of the polymer is 17 to 18 (g/g mole $\times 10^{-6}$) and the degree of hydrolysis is 25%.

The interfacial tension between the model oils and the polymer solution was measured by a spinning drop interfacial tension meter (LP-12, EOR Inc.; Houston, TX, USA) at 24 °C. The interfacial shear viscosities were measured using a SVR-S Interfacial Viscoelastic Meter (Kyowa Kagaku Co. Ltd, Japan) [18] at 25 °C. The zeta potential on the oil droplets was measured by a zeta potential meter (ZPOM, Kyowa Kagaku Co. Ltd, Japan) at 25 °C.

14.3.2 RESULTS AND DISCUSSION

14.3.2.1 Interfacial Tension

Table 14.10 shows that the interfacial tension between the model oils or crude oil and the formation water was not affected by the HPAM, which shows that HPAM is not an interfacially active substance.

14.3.2.2 Interfacial Shear Viscosity

Figures 14.20 to 14.22 show that the interfacial shear viscosity between the resin, asphaltene, or crude model oils and HPAM solution was affected by the concentration of HPAM. The higher the concentration of the polymer, the larger the interfacial shear viscosity. It should be noted that the value of the interfacial shear viscosity of the crude model oil is close to that of the asphaltene model oil system and higher than that of the resin model oil system. This shows that the asphaltene fraction dominates the strength of the interfacial film between the crude oil and HPAM solution.

TABLE 14.9
Composition of Synthetic Formation Water

Ion	Concentration (mg l ⁻¹)
Cl ⁻	2885.49
HCO ₃ ⁻	818.89
Na ⁺ + K ⁺	2064.55
Mg ²⁺	20.88
Ca ²⁺	66.85

TABLE 14.10
Interfacial Tension Between Model Oil and HPAM Solution (mN m^{-1})

HPAM (mg l^{-1})	Model Oil			
	Jet Fuel	Resin Model Oil	Asphaltene Model Oil	Crude Model Oil
0	52.2	17.2	15.2	23.0
25	52.8	24.2	20.4	30.1
50	55.4	27.7	19.1	29.9
100	54.7	26.2	20.6	29.8
200	46.2	22.8	18.7	27.9
300	48.6	24.4	17.8	27.1
400	49.1	17.1	18.2	31.1

Temperature: 24 °C.

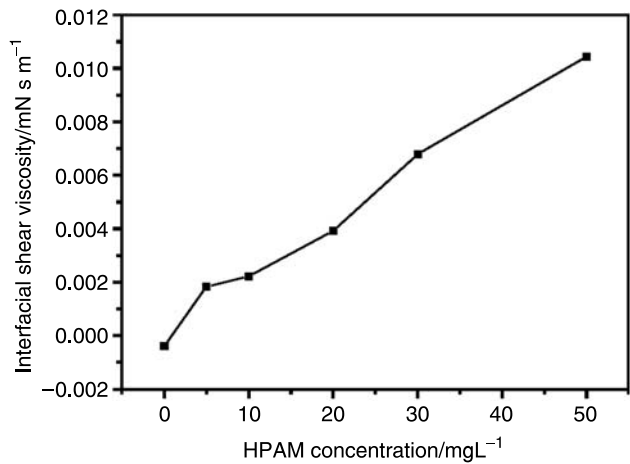


FIGURE 14.20 Interfacial shear viscosity between resin model oil and HPAM solution (oil: 1% resin model oil, water: HPAM solution, T: 25 °C, shear rate: 0.3 rad^{-1}).

This study revealed that HPAM is able to be absorbed at the interface between the model oils and water even when the polymer is not interfacially active and the polymer can enhance the strength of the interfacial film formed by the interfacially active fractions from the crude oil.

14.3.2.3 Zeta Potential

Table 14.11 shows that the absolute value of zeta potential on the resin model oil or asphaltene model oil droplets was increased with the addition of the HPAM. Figure 14.23 shows that the absolute value of zeta potential on the crude oil droplets was also increased as the concentration of HPAM increases. This shows the adsorption of HPAM at the interface between the model oils and water can modify the electrical property of the interface significantly. Therefore, HPAM is able to enhance emulsion stability.

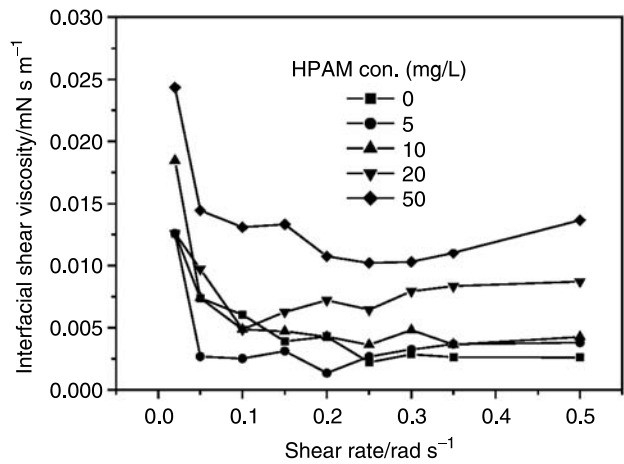


FIGURE 14.21 Interfacial shear viscosity between asphaltene model oil and HPAM solution (oil: 1% asphaltene model oil, water: HPAM solution, T: 25 °C).

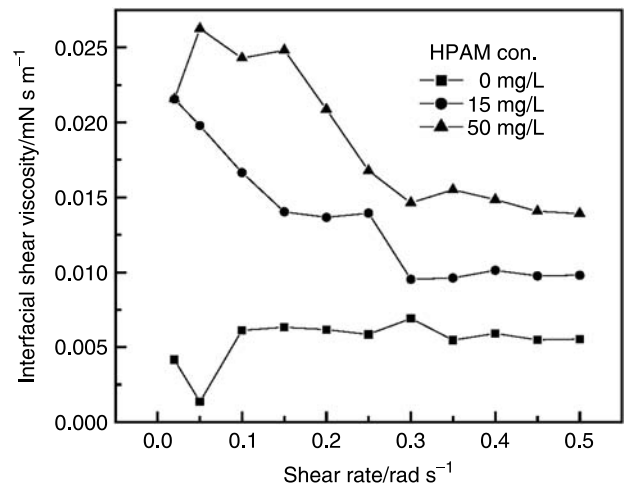


FIGURE 14.22 Interfacial shear viscosity between crude model oil and HPAM solution (oil: 10% crude model oil, water: HPAM solution, T: 25 °C).

14.3.2.4 Stability of O/W Emulsions

Table 14.12 shows that when the concentration of HPAM is in the range 50 to 100 mg/l the amount of oil in the water is much more than when no HPAM has been added to the water. It is clear that the change of electrical properties, caused by HPAM, at the interface between the oil and water contributes to stabilizing the o/w emulsion.

The effect of polymer on the interfacial properties between oil and water is complicated for a simple system and it is much more complex for a crude oil and water system in practice. There are both theoretical and practical problems. From this study it can be said that HPAM can be adsorbed

TABLE 14.11
Zeta Potential on Oil Droplets (mV, 25 °C)

HPAM (mg l ⁻¹)	Oil	
	Resin Model Oil (5 %)	Asphaltene Model Oil (5 %)
0	-11.6	-9.1
50	—	—
100	-15.1	-44.5
200	—	-42.8

TABLE 14.12
The Oil in O/W Emulsion Affected by HPAM (mg l⁻¹)

HPAM Solution (mg l ⁻¹)	5% Resin Model Oil Emulsion	5% Asphaltene Model Oil Emulsion	Crude Emulsion
0	33	40	60
50	100	110	118
100	39	127	99
200	25	49	51

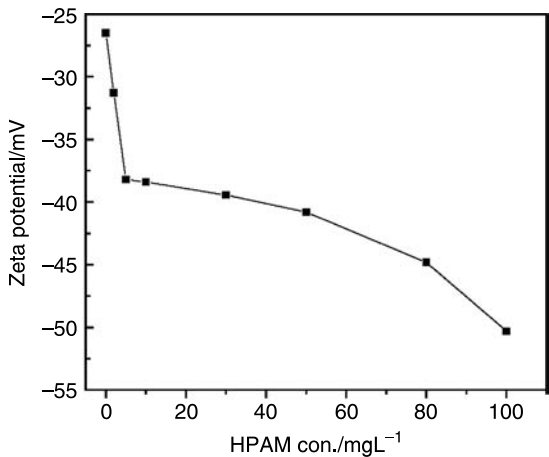


FIGURE 14.23 Influence of HPAM on zeta potential of crude oil droplets (oil: 3% crude model oil, T: 25 °C).

at the interface between the model oils and the synthetic formation water. The adsorption of the polymer increased the interfacial shear viscosity and the strength of the interfacial film between the oil and the water, which enhanced the stability of the emulsion. It is most important that the adsorption of polymer onto the surface of the oil droplets gives the surface a high negative potential. This proved that the oil droplets were not only stabilized by steric stabilization of the polymer but also by electrostatic stabilization. It seems that, in practice, electrostatic stabilization of the polymer dominated the stability of the o/w emulsion.

14.4 EFFECT OF SURFACTANT

14.4.1 EXPERIMENTAL

The interfacially active fractions of asphaltene and resin used in these experiments were separated from Gu Dong 4[#] crude oil. The resin, asphaltene, and crude model oils were prepared with jet fuel. The surfactant used was a petroleum sulfonate (TRS) produced in Sheng Li oil field in China. The aqueous phase used in the experiments was synthetic formation water (Table 14.9) or TRS solution of the water.

The interfacial tension between the model oils and the surfactant solution was measured by a spinning drop interfacial tension meter (LP-12, EOR Inc.; Houston, TX, USA) at 45 °C. The interfacial shear viscosities were measured using a SVR-S Interfacial Viscoelastic Meter (Kyowa Kagaku Co. Ltd, Japan) [18] at 25 °C. The zeta potential on the oil droplets was measured by a zeta potential meter (ZPOM, Kyowa Kagaku Co. Ltd, Japan) at 25 °C.

14.4.2 RESULTS AND DISCUSSION

14.4.2.1 Interfacial Tension

Table 14.13 shows the interfacial tension between the model oils and TRS solution or the synthetic formation water. It is clear that the interfacial tension was decreased dramatically with the addition of the surfactant.

14.4.2.2 Interfacial Shear Viscosity

The interfacial shear viscosity between resin model oil and the surfactant solution is shown in Figure 14.24. The interfacial shear viscosity was reduced with the addition of the surfactant; the higher the concentration of the surfactant the lower the interfacial shear viscosity.

Figure 14.25 shows that the interfacial shear viscosity between asphaltene model oil and the surfactant solution was increased as the concentration of the surfactant increased from 0 to 0.3%, and the interfacial shear viscosity reduced again when the concentration of the surfactant is 0.5%. Figure 14.26 shows a similar result as shown in Figure 14.25, although the value of the interfacial shear viscosity of crude model oil system is less than that of the asphaltene model oil system and higher than that of the resin model oil system. This proves that the strength of the interfacial film between the crude oil and the surfactant solution is dependent on both the asphaltene and resin fractions.

TABLE 14.13
Interfacial Tension Between Model Oils and TRS Solution (mN m⁻¹), T: 45 °C

Model Oil	TRS (%)			
	0	0.1	0.3	0.5
3% Crude oil	8.5803	0.989	0.0168	0.0099
3% Asphaltene oil	4.3884	0.118	0.0066	0.0012
3% Resin oil	6.8538	0.0212	0.00816	0.0013

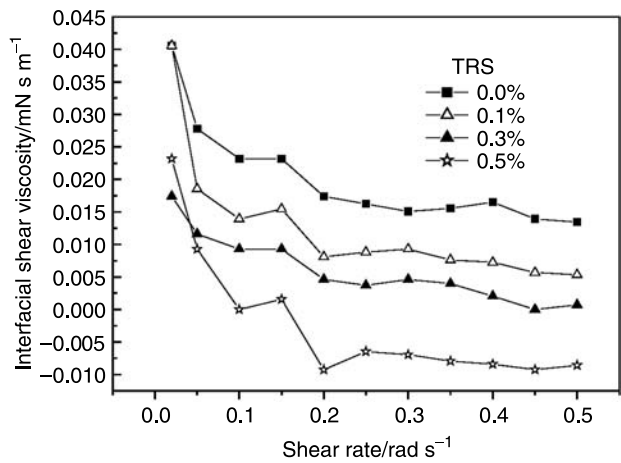


FIGURE 14.24 Interfacial shear viscosity between 3% resin model oil and TRS solution, 25 °C.

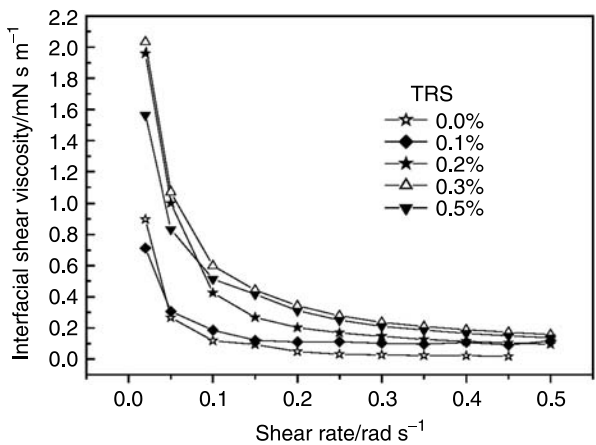


FIGURE 14.25 Interfacial shear viscosity between 3% asphaltene model oil and TRS solution, 25 °C.

14.4.2.3 Zeta Potential

The zeta potential on oil droplets changed with concentration of TRS for resin, asphaltene, and crude model oils is shown in [Figures 14.27 to 14.29](#). The absolute value of zeta potential for resin model oil is increased from 0 to 0.1% of TRS in distilled water. Then the absolute value of zeta potential was reduced when the concentration of TRS is higher than 0.1%.

[Figure 14.28](#) shows the absolute value of zeta potential on asphaltene model oil droplets is increased fast from 0 to 0.05% of TRS in distilled water. Then the absolute value of zeta potential was increased slowly when the concentration of TRS is higher than 0.05%. It is interesting that the change in the absolute value of zeta potential on crude model oil droplets is a combination of the resin and asphaltene model oils ([Figure 14.29](#)). It shows that the electrical property of the

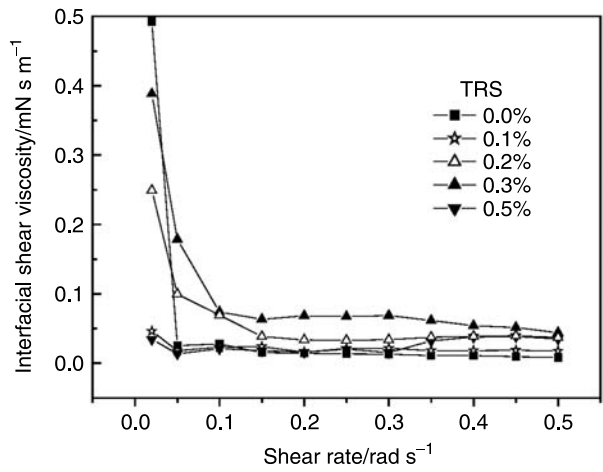


FIGURE 14.26 Interfacial shear viscosity between 3% crude model oil and TRS solution, 25 °C.

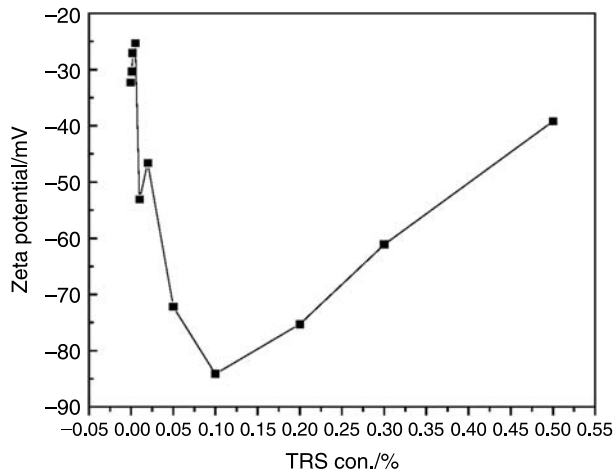


FIGURE 14.27 Influence of TRS on zeta potential (oil: 3% resin model oil, T: 25 °C).

interface between crude model oil and the surfactant solution is also dependent on the asphaltene and resin fractions.

Based on this study it is important to know that the adsorption of the surfactant at the interface between the model oils and distilled water makes the oil droplets negatively charged; the formation of an electrical double layer is able to enhance the stability of o/w emulsions.

14.4.2.4 Stability of Emulsions

The stability of the emulsion studied in this work is evaluated by the value of a volume fraction of $(V_t - V_0)/V_0$. V_t presents the volume of w/o emulsion, V_0 presents the volume of the oil added.

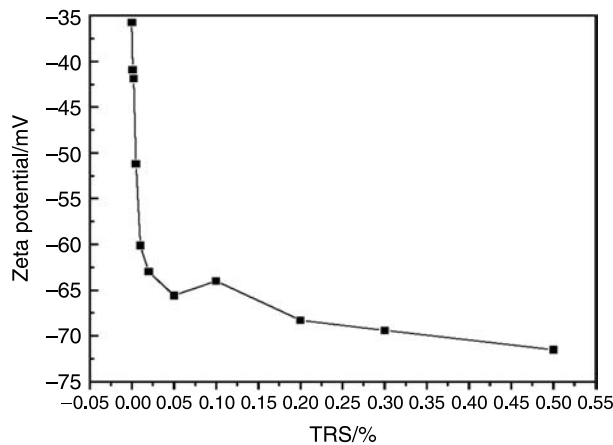


FIGURE 14.28 Influence of TRS on zeta potential (oil: 3% asphaltene model oil, T: 25 °C).

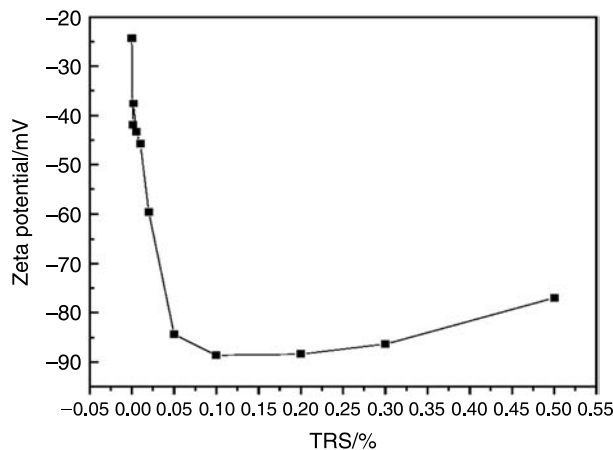


FIGURE 14.29 Influence of TRS on zeta potential (oil: 3% crude model oil, T: 25 °C).

When $(V_t - V_0)/V_0 > 0$, the emulsion is the w/o type. When $(V_t - V_0)/V_0 < 0$, the emulsion is the o/w type, and when $(V_t - V_0)/V_0 = 0$, the emulsion is broken completely.

Figure 14.30 shows the emulsion formed with resin model oil and TRS solution is o/w type, and the time of $(V_t - V_0)/V_0$ changed from -1 to 0 was increased obviously as the concentration of TRS increased. This reveals that the stability of the emulsion was enhanced as the concentration of TRS was increased.

Figure 14.31 shows the emulsion formed with asphaltene model oil and the synthetic formation water is the w/o type. However, the emulsion was changed from the w/o to the o/w type as the concentration of TRS was increased from 0 to 0.5% . As the asphaltene fraction is oil soluble, the interfacially active substance and TRS is a strong water soluble surfactant. This result shows that the emulsion type is dependent on the effect of asphaltene and TRS, and TRS plays an important role when the concentration of the surfactant is high.

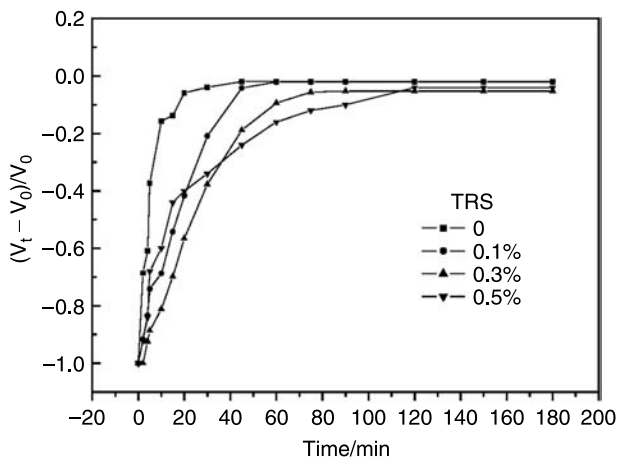


FIGURE 14.30 Stability of emulsion formed with 3% resin model oil and TRS solution, 30 °C.

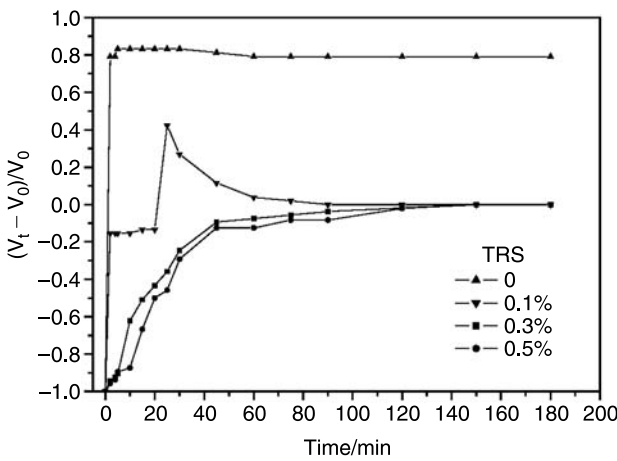


FIGURE 14.31 Stability of emulsion formed with 3% asphaltene model oil and TRS solution, 30 °C.

Figure 14.32 shows the stability of the emulsion formed with crude model oil and TRS solution. The emulsions are the o/w type and the emulsion has a higher stability when the concentration of TRS is 0.3%. It seems that the resin fraction dominates the properties of the emulsion when TRS was added in the water.

14.5 EFFECT OF ALKALINE-SURFACTANT-POLYMER

In this work the experimental methods and condition are the same as described in Section 14.4.1.

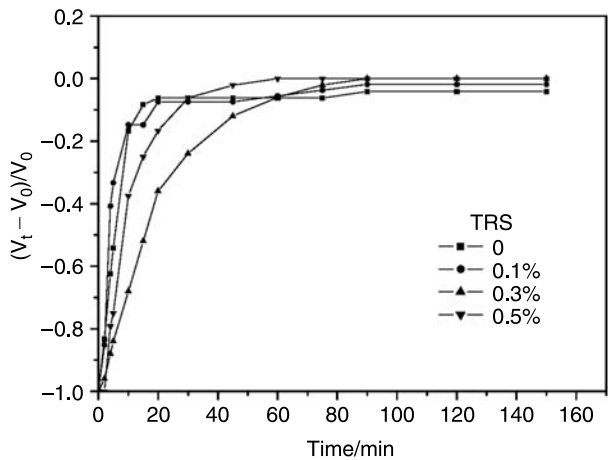


FIGURE 14.32 Stability of emulsion formed with 3% crude model oil and TRS solution, 30 °C.

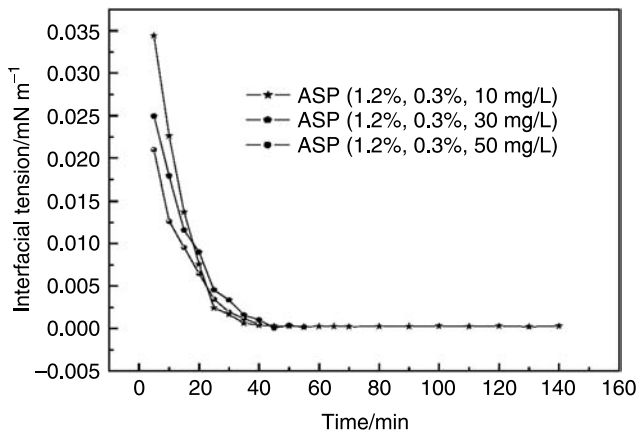


FIGURE 14.33 Interfacial tension between 3% crude model oil and ASP solution (A – Na₂CO₃, S – TRS, P – HPAM, crude Gu Dong 4[#], T: 45 °C).

14.5.1 INTERFACIAL TENSION

Figure 14.33 shows that when Na₂CO₃ (1.2%), HPAM (10 mg/l), and TRS (0.3%) were added at the same time the interfacial tension between crude model oil (Gu Dong 1[#]) and the solution is very low. It is obvious that the coordination effect of Na₂CO₃ and TRS make the main contribution to decreasing the interfacial tension.

14.5.2 INTERFACIAL SHEAR VISCOSITY

Figure 14.34 shows the interfacial shear viscosity between crude model oil (Gu Dong 4[#]) and SP solution. Before the measurement the crude model oil had been reacted with 1.2% Na₂CO₃ solution for 10 days to form sufficient interfacially active components. The result shows when

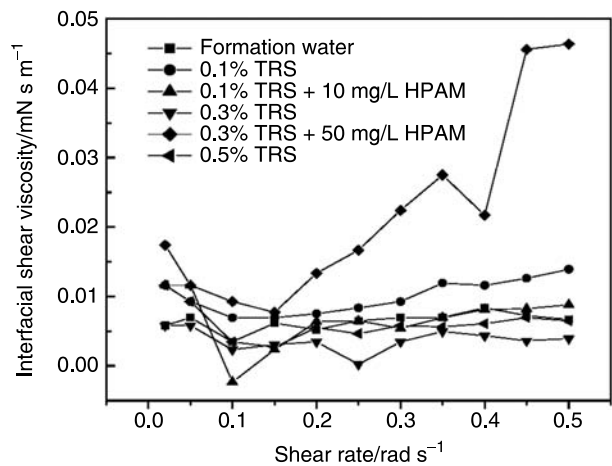


FIGURE 14.34 Interfacial shear viscosity between 0.1% crude model oil (had been reacted with 1.2% Na₂CO₃ solution for 10 days) and SP solution (S – TRS, P – HPAM, crude Gu Dong 4[#], T: 25 °C).

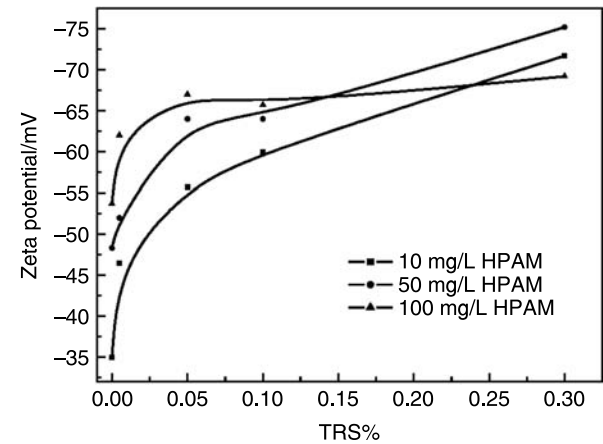


FIGURE 14.35 Influence of ASP on zeta potential (3% crude model oil (Gu Dong 4[#]) had been reacted with 1.2% Na₂CO₃ solution for 1 day, T: 25 °C).

the concentration of HPAM is 50 mg/l the polymer makes a main contribution to interfacial shear viscosity under the experimental condition. It should be noted that the interfacial shear viscosity is increased as the shear rate increases when the aqueous phase contains 0.3% TRS and 50 mg/l HPAM. It seems that there may be some particles formed at the interface [18].

14.5.3 ZETA POTENTIAL

Figure 14.35 shows the zeta potential on crude model oil droplets changed with concentration of TRS and HPAM. Before the measurement the crude model oil had been reacted with 1.2%

Na₂CO₃ solution for 1 day to form sufficient interfacially active components. The results show that the zeta potential increased rapidly when the concentration of TRS was below 0.05%, and did not change much when the concentration of TRS was higher than 0.05%. This may be caused by the equilibrium adsorption of TRS on the interface. It can also be seen that the higher the concentration of HPAM in the solution the larger the zeta potential. It is clear that there were more HPAM molecules adsorbed on the interface when the concentration of HPAM was increased.

14.5.4 STABILITY OF EMULSIONS

The stability of the emulsions formed with crude model oil and SP solution is shown in Figure 14.36. Before determination of the emulsion stability the crude model oil had been reacted with 1.2% Na₂CO₃ solution for 1 or 10 days to form sufficient interfacially active components in part of the experiments. It is very interesting that the emulsion formed with 3% crude model oil and the solution contains 0.1% TRS and 10 mg/l HPAM is the most stable in the experimental condition, and when the concentration of HPAM increased from 10 to 50 mg/l the stability of the emulsion decreased. When crude model oil had been reacted with Na₂CO₃ for 10 days the stability of the emulsion formed with the oil and the solution containing 0.1% TRS and 50 mg/l HPAM is most unstable. The stability of the emulsions formed with the crude model oil that had been reacted with Na₂CO₃ for 1 day and the solution contains 0.1% TRS and 10 to 50 mg/l HPAM is in the middle case. It should be noted that all the emulsions are the o/w type; therefore, electrical double layer stabilization might be one of the main mechanisms for stabilizing the emulsions. When the crude model oil reacted with Na₂CO₃ interfacially active components are formed. Because these interfacially active components are more oil soluble the components might act as demulsifiers to decrease the stability of the o/w emulsions. For longer reaction times, more interfacially active components are formed, and the emulsions are more unstable. The effect of HPAM in these experiments is very complicated. HPAM may be adsorbed at the interface and increase the strength of the interfacial film. The absolute value of the zeta potential

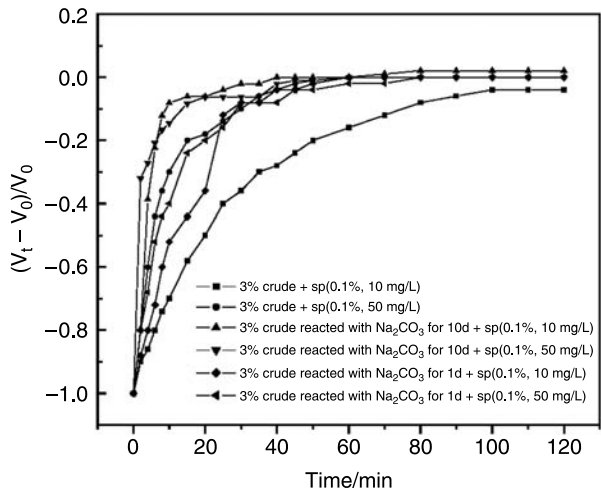


FIGURE 14.36 Stability of emulsion formed with 3% crude model oil and ASP solution (A – Na₂CO₃, S – TRS, P – HPAM, crude Gu Dong 4[#], T: 45 °C).

may be increased, and therefore HPAM is able to enhance the stability of the emulsion. However, HPAM is also able to flocculate the oil drops and decrease the stability of the emulsions. In this experiment the effect of flocculation seems to play an important role, because the stability of the emulsions decreased when the concentration of HPAM was increased.

14.6 CONCLUSION

Based on this study the following conclusions can be drawn:

1. The asphaltene fractions from Gu Dong crude oils of high acid number have more polar, larger, acidic components than the other fractions. The components that react with Na_2CO_3 are able to form interfacially active components that accumulate at the oil/water interface and form a rigid film around water droplets. The asphaltene fraction from Gu Dong crude oils dominates the stability of the emulsions of the crude and Na_2CO_3 solution.
2. It is not only acidic oxygen compounds but also esters in the saturated fractions from paraffinic Da Qing crude oil of low acid number that, when reacted with NaOH , produce components in the reaction which are responsible for stabilizing the emulsions of the crude oil and NaOH solution. The reaction takes place over a long time and the ASP flooding process in the reservoir provides sufficient time for the formation of soap-like components by the reaction of the alkaline and acidic or nonacidic components in the saturation fraction.
3. The effect of HPAM on the formation of the crude oil emulsion in ASP flooding is very complicated. HPAM may be adsorbed at the interface and increase the strength of the interfacial film and the absolute value of zeta potential, therefore enhancing the stability of the emulsion. However, HPAM is also able to flocculate the oil droplets and decrease the stability of o/w emulsions.
4. It is important to know that the adsorption of HPAM, TRS surfactant, and the interfacially active components formed in the reaction of Gu Dong and Da Qing crude oils and the alkali at the interface between the model oils and distilled water makes the oil droplets negatively charged and enhance the stability of o/w emulsions.
5. The formation and properties of the crude emulsions formed in ASP flooding are extremely complicated. They not only depend on the properties of the crude oil, the injection water and formation water, the alkali, HPAM, and surfactant used, but also on the properties of the reservoir formed alkali-oil surfactant, the time of the chemical solution flood through the reservoir, the reactions of the alkali, HPAM, and surfactant with the reservoir, and the solid particles from the reservoir, for example. Studies in this field are just beginning, and we have a long way to go before we understand the scientific nature of the emulsions.

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