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Role of polar compounds in crude oils on rock wettability

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ABSTRACT

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The main objective of this research was to study the effect of polar compounds present in some Saudi crude oils on rock wettability.

It was found that the contact angle increases with increasing percentage of polar compounds in crude oil at 22°C. A minimum contact angle, however, was obtained at 2.7 wt% polar compounds at 50°C. Increasing temperature tends to make the core sample oil-wet, in both cases of using crude oils or their fractions.

Introduction

The effect of crude oil components on rock wettability was studied for both sandstone and limestone cores by Denekas et al. (1959). They demonstrated that the wettability of a sandstone may be governed by the concentration of the surfactants in the crude oil. Limestone reservoir rocks, on the other hand, appear to be particularly sensitive to basic nitrogenous surfactants. Cuiec (1986) confirmed that carbonate rock has the ability to have more interactions than sandstone with the components of crude oil.

Extensive laboratory experience (Donaldson and Crocker, 1980; Donaldson, 1981; Anderson, 1986) has led to the conclusion that the nature of the reservoir wettability is due to the absence or presence of polar compounds, apparently asphaltic in nature, adsorbed on the rock surfaces, and which tend to make these surfaces oil-wet. The effect of these polar compounds depends to some degree upon the nature of the rock surfaces, that is, upon whether the rock surfaces are predominantly silica, carbonate or clay. The effects of wettability problems are more pronounced in carbonate than in sandstone reservoirs (Trieber et al., 1972; Chilingar and Yen, 1983; Cuiec, 1984).

Several researchers (Croker and Marchin, 1988) have indicated that the wettability of a reservoir rock is strongly related to the amount of adsorption by the heavy ends, found in the crude oil. The heavy ends contain the most polar compounds found in the crude oils and constitute principally asphaltene and resin fractions. One approach to gain insight into wettability has been to perform adsorption studies of crude oil and oil components on reservoir rock and minerals (Anderson, 1986). The behavior of a particular fraction separated from a given crude oil can be different than that when it is associated with other fractions (Cuiec, 1986).

All of the six polar and three asphaltene fractions tested by Crocker and Marchin (1988) caused the wettability to be shifted toward a more oil-wet (less water-wet) state. One of the polar fractions caused a change in wettability of 0.87 (USBM wettability index var-

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ies from $+\infty$ for complete water wetness to $-\infty$ for complete oil wetness)* (Anderson, 1986). Attempts have been made to relate various constituents or overall gross chemical composition of a crude oil to its wettability. Cuiec (1984) noted some correlation between wettability and elemental sulfur content, which he attributed to the correlation between the content of asphaltenes and wettability.

Extensive research work done by Chilingar and Yen (1983) indicated that increasing carbonate content in a reservoir rock will increase the relative permeability to oil. The same was true with increasing concentration of polar substances in oil.

In a previous work, Sayyouh et al. (1990a) studied the effects of acidity and alkalinity on wettability. It was found that the contact angle increases with increasing Saudi crude oil acidity for all NaOH concentrations used. When the pH was alkaline, the rock surface tended to be oil-wet.

In another paper, Sayyouh et al. (1990b) investigated the effect of clay mineralogy, salinity and alkalinity on wettability. The contact angle increased with increasing clay content, depending on the solution salinity and alkalinity.

The main objective of this research was to study the effects of some active constituents of Saudi crude oils on rock wettability.

Experimental work

Five different Saudi crude oils and their fractions were used in this work. Sandstone cores obtained from wells in the Saudi Aramco production area in the eastern region of the Kingdom were used.

In all measurements of contact angle, Safaniyah, light, medium, heavy, and Abu Safah crudes (and their fractions) were used. Sandstone core samples used had compositions shown in Table 1.

TABLE 1

Mineralogical composition of some Saudi sandstone and limestone cores

	Quartz (% wt)	Feldspar (% wt)	Other minerals (% wt)	Clays (% wt)
Al Khafji (1) Sandstone	94.8	2	1.0	2.2*
Al Khafji (2) Sandstone	92.0	2	1.0	5.0*
Saudi Aramco Sandstone	85.0	3	4.0	8.0**
Saudi Aramco Limestone	traces	–	–	6.0***

*65% kaolinite and 35% chlorite.
**52% kaolinite, 27% chlorite, 15% illite and 6% montmorillonite.
***98% kaolinite.

Apparatus

Figure 1 shows a schematic diagram of the apparatus used in measuring the contact angle between oil and water at different temperatures of 22°, 50° and 70°C. The apparatus consists of the following items: (a) core holder, where the core can be placed and fixed; (b) glass reservoirs for oil and water; (c) temperature control system; and (d) saturation setup, which is used to saturate the core plugs with solutions under vacuum. A camera with normal film was used to take photos of the oil droplet.

Procedure

The wettability measurements were made by the contact angle method in the absence of air and metal parts in the apparatus. It was found previously (Treiber et al., 1972; Chilingar and Yen, 1983) that wettability tests are extremely sensitive to air and contamination, especially aeration and introduction of trace metals. Presence of trace metals and oxidation renders the cores water-wet.

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* $+1$ = strongly water-wet; -1 = strongly oil-wet.

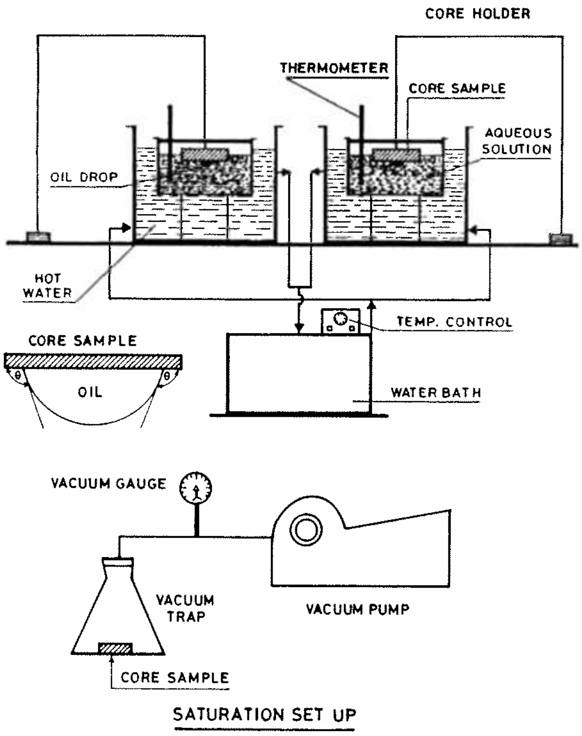

Fig. 1. Contact angle measurement apparatus.

Samples 1.5 inch (3.81 cm) in diameter and 1 inch (2.54 cm) long with a very smoothed surface were used. Morrow (1975) found that the apparent contact angle for smooth and rough sphere packs differ. The samples were treated as described by Cuiec (1975) and Cuiec et al. (1979). Toluene saturated with water and methanol plus toluene mixtures were used for cleaning the samples. Drying was done under controlled humidity. The samples were then evacuated and saturated with the aqueous solution.

The oil droplet was put in contact with the downward surface of a core sample and then immersed in the aqueous solution in a glass container. The oil droplet was photographed at different time intervals to investigate the change of the contact angle with time, until equilibrium was reached. Equilibrium was attained when no change in the shape of oil drop was observed. Equilibrium time was about 24 h.* The contact angle measured in the water phase was determined by making a tangent to both sides of the oil droplet. The precision obtained when evaluating the contact angle through the tangent obtained on the photograph was within ±1°.

Results and discussion

The wettability of a reservoir rock is thought to be dependent on the extent of adsorption of heavy ends (Clementz, 1977). It appears that the adsorption of heavy ends will affect the surface distribution of the fluids in the porous medium. The manner in which adsorption of heavy ends affect the magnitude of the surface saturation of fluids on the reservoir rock is not yet known. A summary of the contact angle measurements is shown in Table 2.

Effect of polar compounds on wettability

Saudi crude oils studied in the present work (Abu Safah, light, medium, heavy, and Safaniyah) were classified according to the U.S. Bureau of Mines method (Nelson, 1958). This method is based on a modified Hempel distillation of the crude oil and upon the API gravity of certain fractions obtained during distillation. The distillation was conducted at two different pressures: atmospheric pressure and an absolute pressure of 40 mm Hg. Figures 2 and 3 show the distillation curves of Saudi crude oils at atmospheric pressure and an absolute pressure of 40 mm Hg, respectively. Application of the U.S. Bureau of Mines method to Saudi crude oils reveals that these crudes are paraffin-wax-bearing. Based on the initial and final boiling points of wax distillates, which were recovered under vacuum conditions, the volume percentages of these distillates were determined from the true boiling point curves

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*In the opinion of E.C. Donaldson, 24 h is not a sufficient time for equilibration and more than 100 h is required for proper equilibration at each temperature. (Editorial comment — G.V.C.)

TABLE 2

Contact angle data

Run	Water type	Rock type	Temperature (°C)	Crude	$\theta_{\text{Equ.}}$*
1	Distilled	Sandstone	22	Abu Safah	129
2	Distilled	Sandstone	22	Light	113
3	Distilled	Sandstone	22	Medium	132
4	Distilled	Sandstone	22	Heavy	140
5	Distilled	Sandstone	22	Safaniyah	123
6	Distilled	Sandstone	50	Abu Safah	115
7	Distilled	Sandstone	50	Light	95
8	Distilled	Sandstone	50	Medium	110
9	Distilled	Sandstone	50	Heavy	140
10	Distilled	Sandstone	50	Safaniyah	120
11	35,000 ppm NaCl	Sandstone	22	Abu Safah	80
12	35,000 ppm NaCl	Sandstone	50	Abu Safah	133
13	35,000 ppm NaCl	Sandstone	70	Abu Safah	137
14	Distilled	Sandstone	22	Abu Safah (121-204)	104
15	Distilled	Sandstone	22	Heavy (121-204)	85
16	Distilled	Sandstone	22	Safaniyah (121-204)	80
17	Distilled	Sandstone	50	Abu Safah (121-204)	120
18	Distilled	Sandstone	50	Light (121-204)	90
19	Distilled	Sandstone	50	Heavy (121-204)	78
20	Distilled	Sandstone	50	Safaniyah (121-204)	68
21	Distilled	Sandstone	22	Abu Safah (82-121)	113
22	Distilled	Sandstone	22	Light (82-121)	100
23	Distilled	Sandstone	50	Abu Safah (82-121)	130
24	Distilled	Sandstone	50	Light (82-121)	92
25	Distilled	Limestone	22	Safaniyah	55
26	10% NaCl	Limestone	22	Safaniyah	110

*θ = equilibrated contact angle.

shown in Fig. 3; data are presented in Table 3. The percentages of polar compound fractions in these crudes are given in Table 4 for light, medium and heavy crudes. The latter three were selected based on their API gravities. An

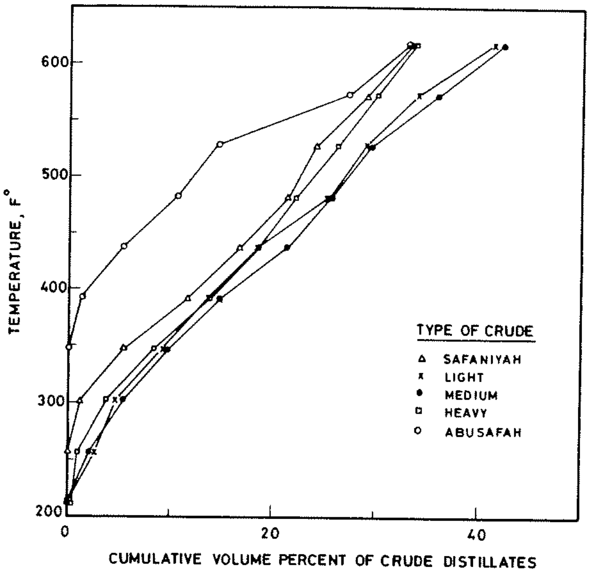

Fig. 2. Results of atmospheric distillation of Saudi crude oils.

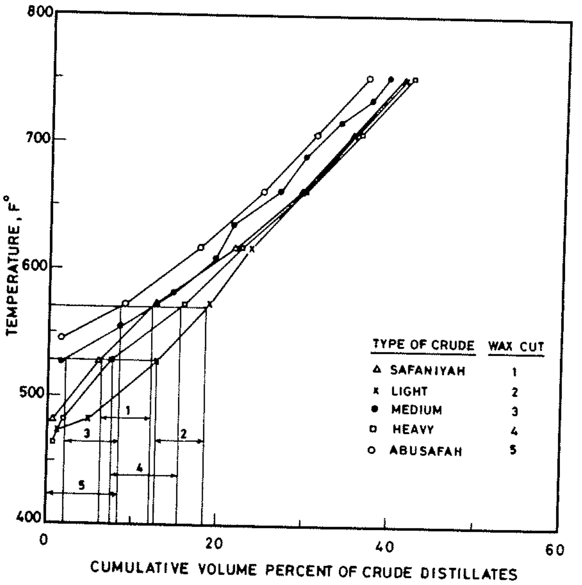

Fig. 3. Results of vacuum distillation of Saudi crude oils.

NaCl solution (35,000 ppm) was used as an aqueous phase.*

The percentages of polar compound fractions were plotted against the contact angle at temperatures of 22° and 50°C in Figs. 4 and 5. Figure 4 shows that, at 22°C, the contact angle increases as the percentage of polar compounds increases. The adsorption from the oil phase of surface-active compounds and retention at the interface because of their polar groups is affected by many variables, such as the ionic composition of water, the potential at the interface, and contents and types of water-soluble matter in the crude oil.

Figure 5, however, shows a minimum contact angle at 2.7 wt% polar compounds at 50°C when using a 0.5 and 1.0% NaOH in 35,000-ppm NaCl aqueous solution. Indeed, several constituents of crude oil have a polar nature, such as asphaltic compounds and natural surfactants. The presence of these compounds may affect the behaviour of magnitude of contact angle at 50°C.

Due to the presence of NaCl, adsorption of ions (inorganic) at the water–oil interface may occur, leading to a layer of pure water, the thickness of which is inversely proportional to the ionic concentration. As a result, electrostatic effects and, consequently, adsorption of surface-active agents may become more pronounced as the ionic concentration is increased. It can also be observed that at a constant percentage of polar compounds, the contact angle increases as the temperature increases.*

Effect of temperature on wettability

Figure 6 shows that increasing temperature tends to make the core oil-wet for Abu Safah crude oil using 35,000-ppm NaCl solution. As shown in this figure, the contact angle increases with increasing temperature up to 50°C, after which a small change is observed. This behavior may be due to the adsorption of the wettability-alternating compounds of the

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*Reconstituted formation water would have been better. (Editorial comment — G.V.C.)

*Inasmuch as numerous researchers observed that increase in temperature causes systems to become more water-wet, the authors request formal discussion of this subject by Drs. N.R. Morrow, F.G. McCaffery, E.C. Donaldson, L. Cuiec and G.V. Chilingarian.

TABLE 3

Physical properties of different crude oils

Crude oil (from Saudi fields)	Specific gravity	Surface tension (dyne/cm)	API	Flash point temperature (°C)	Pour point (°C)	Cloud pont (°C)	Separated volume under vacuum distillation (%)		
							gas oil	wax distillate	bottoms
Abu Safah	0.855	28.7	33.970	21	−4	2	7.0	12.6	80.0
Light	0.850	28.8	34.970	18	−22	−16	15.4	5.6	81.0
Medium	0.870	27.6	31.143	19	−25	−17	6.0	10.0	84.0
Heavy	0.885	30.4	28.000	23	−3	0	8.4	16.6	75.0
Safaniyah	0.560	28.1	33.030	20	−2	2	−	8.6	91.4

TABLE 4

Contact angle versus wt% of polar compounds at 22° and 50°C

Crude	Polar compounds (wt%)	Contact angle (degrees)	Temperature (°C)
Light	1.91	113	22
Light	1.91	95	50
Medium	2.709	132	22
Medium	2.709	110	50
Heavy	2.967	140	22
Heavy	2.967	140	50

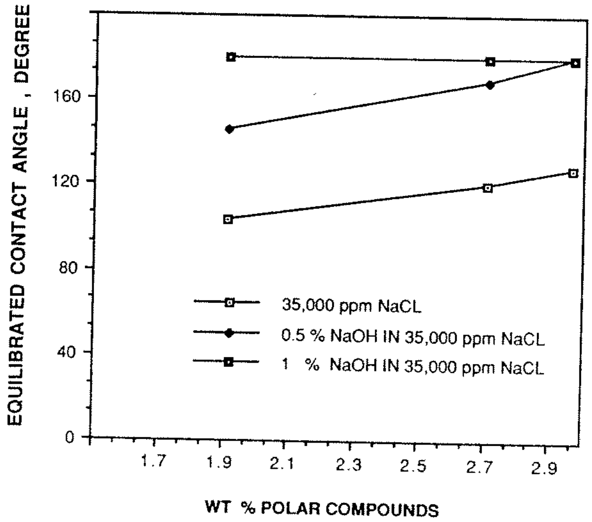

Fig. 4. Effect of polar compounds (wt%) on contact angle at 22°C.

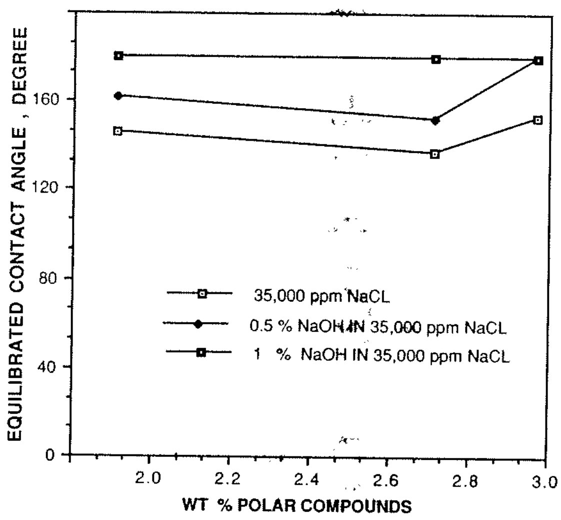

Fig. 5. Effect of polar compounds (wt%) on contact angle at 50°C.

crude on the surface at higher temperatures. The same behavior was noticed previously (Sayyouh et al., 1990a).

Increasing temperature may change the rheological properties and thermodynamic properties of the surface layer. A change in the molecular nature of the surface of the solid phase (e.g., owing to adsorption of the surface-active components of oil due to the increase in temperature) may result in a change in the value and even the sign of the contact angle. When using distilled water, however, increasing temperature tends to make sandstone water-wet, as seen in Figs. 7 and 8. This behavior may be attributed to the increase in

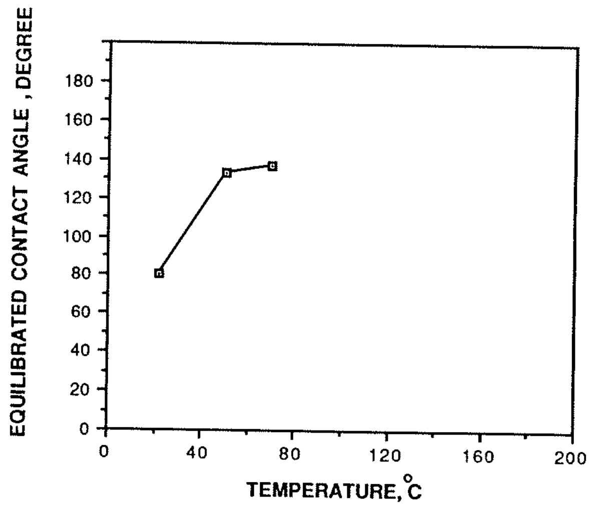

Fig. 6. Equilibrated contact angle versus temperature for Abu Safah crude oil using 35,000 ppm NaCl.

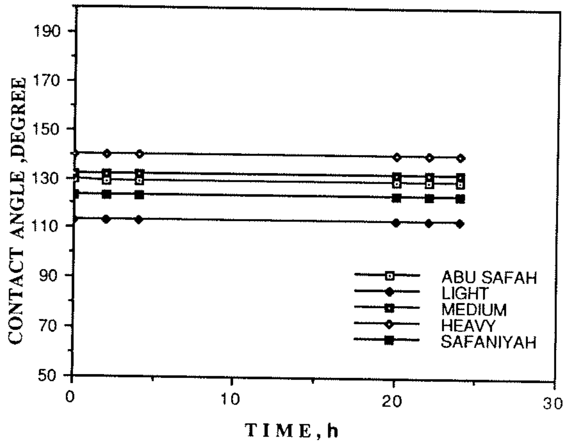

Fig. 7. Contact angle versus time for Saudi crude oils in distilled water at 22°C (after Sayyouh et al., 1990a).

the solubility of wettability-alternating compounds by increasing temperature.

Crude oils versus their fractions

Figures 9 and 10 represent the results of contact angle measurements for different oil cuts (Abu Safah, light, heavy, and Safaniyah) at 121°–204°C, using distilled water at 22° and 50°C. Figures 7 and 8 show the contact angle for different crude oils at 22° and 50°C.

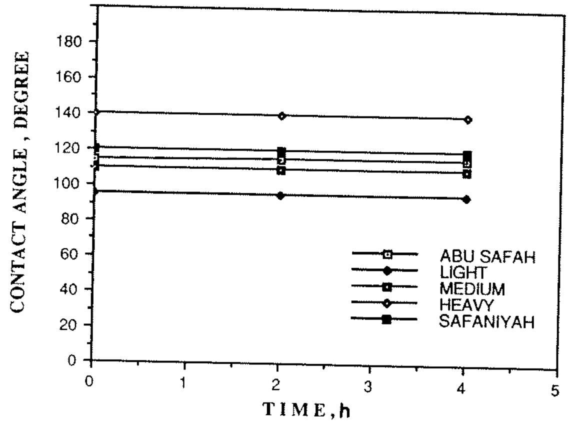

Fig. 8. Contact angle versus time for different crudes using distilled water at 50°C (after Sayyouh et al., 1990a).

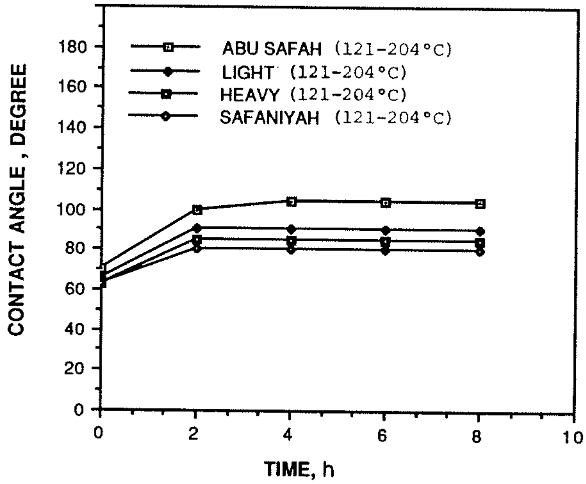

Fig. 9. Contact angle versus time for different fractions using distilled water at 22°C.

It is shown in Figs. 9 and 10, that an equilibrated contact angle behaves similarly for all fractions at both 22° and 50°C. This, however, was not observed when using crude oils, as shown in Figs. 7 and 8.

Figure 11 shows the results of contact angle measurements for Abu Safah 82°–121°C fraction, when using distilled water at 22° and 50°C. The increase in temperature tends to make the core more oil-wet.

Figure 12 represents the results of contact angle measurements for the light crude fraction (82°–121°C) using distilled water at both 22° and 50°C. It is seen that the change of contact angle in this case is small.

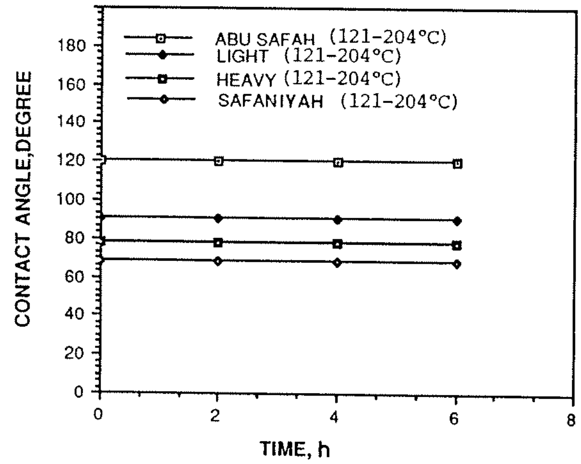

Fig. 10. Contact angle versus time for different fractions using distilled water at 50 °C.

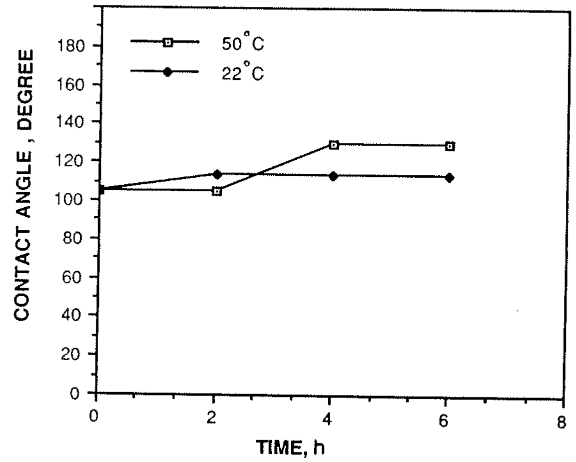

Fig. 11. Contact angle versus time for Abu Safah fraction (82°-121 °C) using distilled water.

All crude oils contain active materials. Crudes can differ greatly, however, with respect to the types, concentrations and states of aggregation of surface-active materials present. That surface-active materials occur in crude oils are evidenced by the fact that interfacial tension between oil and water, or oil and brine is lower with crude oils than with refined oils.

The use of "polar compounds contents" may have some limitations (i.e., two different crude oils with the same content of polar compounds may give different contact angles for a given rock). What is important is the exact composition of the polar fraction (Cuiec, 1984).

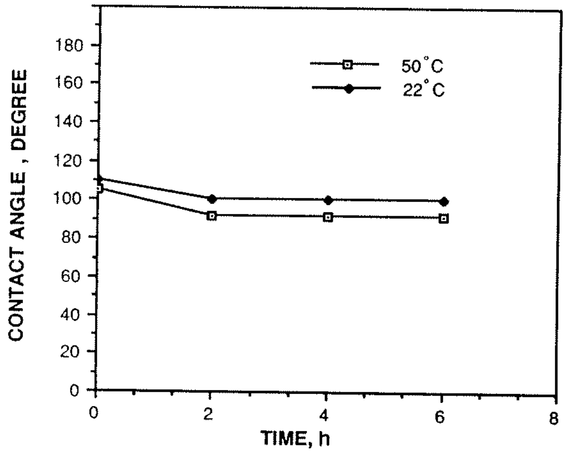

Fig. 12. Contact angle versus time for light fraction (82°-121 °C) using distilled water.

Conclusions

Based on the experimental conditions used in this work the following conclusions can be obtained:

(1) At 22 °C, the contact angle increases with the increase of polar compounds in crude oil.

(2) A minimum contact angle was noticed at 2.7 wt% polar compounds at 50 °C.

(3) Increasing temperature tends to make the core oil-wet, using both oil cuts and crude oils.

(4) The contact angle increases with increasing temperature. Above 50 °C, only a small increase in contact angle was observed.

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