Crude Oil/Brine Contact Angles on Quartz Glass

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ABSTRACT

The initial wettability of a reservoir is the result of complex interactions between the crude oil, the connate water, and the rock surfaces. Adsorption of heavy polar organic material, commonly identified with the asphaltenes in crude oil, is responsible for alteration of wetting properties of the rock. Measurements of contact angles provide a convenient and conceptually simple approach to quantification of the wettability given by oleic/aqueous liquid pairs at a smooth mineral surface. Flat quartz surfaces are often used as a representative surface for sandstones.

This study reports changes in wetting induced by adsorption from crude oil on quartz glass by brine/crude oil pairs. Wilhelmy plate wettability measurements were made with either crude oil or a refined oil as the oleic phase. Wettability changes induced by an asphaltic crude oil were much greater than those given by its maltenes or by a crude oil with very low asphaltene content. Brine compositions included solutions of sodium chloride, three synthetic reservoir brines, and ten- and hundred-fold dilutions of the reservoir brines. Contact angles decreased with increase in brine concentration and with increasing temperature of measurement. Contact angle results are compared with changes of wettability in Berea sandstone and in synthetic cores exposed to brine and crude oils.

INTRODUCTION

The wettability of strongly water-wet surfaces can be changed by contact with crude oil (Cuiec, 1991). Adsorption of heavy polar components, commonly identified with asphaltenes from crude oil, is the main cause of wetting alteration (Benner and Bartell, 1941; Collins and Melrose, 1983; Clementz, 1982; Dubey and Waxman, 1991). This alteration is the result of complex interactions between the crude oil, the brine phase and the rock surface that affect adsorption of crude oil components. The purpose of the present work is to explore wetting alteration by adsorption from crude oils onto quartz surfaces overlain by brine or coated with a brine film.

EXPERIMENTAL PROCEDURES

Quartz plate preparation. Rectangular plates of quartz glass were used as the solid substrate. The plates were cleaned with a detergent solution, washed with distilled water, and agitated ultrasonically in a 30% H_2O_2 + 20% NH_4OH (9:1) cleaning solution for 30 minutes. The plates were left to soak overnight, and then rinsed thoroughly with distilled water. After cleaning, the plates were determined to be strongly water-wet from observation of a wetting film and measurements of receding and advancing contact angles of zero for clean decane and distilled water or brine (Mennella *et al*, 1995).

Fluids. The properties of three synthetic reservoir brines are listed in **Table 1**. Three crude oils were used in this study (**Table 2**). Maltenes were prepared from heptane de-asphalted A'93 crude oil (40:1 vol/vol). All of the oils were filtered and some light ends were removed by evaporation. The n-decane used as the probe oil in some measurements was purified by flow through packed columns of silica gel and alumina.

Table 1. Composition of synthetic reservoir brines

Brine	K^+ (ppm)	Na^+ (ppm)	Ca^{2+} (ppm)	Mg^{2+} (ppm)	Cl^- (ppm)	HCO_3^- (ppm)	SO_4^{2-} (ppm)	I (*M*)	pH
PB	52	8,374	110	24	13,100	-	-	0.4	6.8
DG*	7,237	4,267	218	32	13,414	-	-	0.4	7.0
CS	56	5,626	58	24	8,249	1,119	18	0.3	7.8

* KCl originates from clay stabilization treatment for injected brine

Table 2. Reservoir temperatures T_{res} and oil properties at 25°C

Oil	T_{res}(°C)	Density(g/mL)	Viscosity (cP)	C_7-asphaltenes (wt%)
A'93	80	0.895	39.3	4.0
A'95	80	0.909	44.9	6.6
CS	55	0.886	69.0	0.8

Test procedures. Two experimental test sequences, identified as clean plate or crude-oil treated plate procedures, are illustrated in **Fig. 1**. For the clean plate procedure, quartz plates were soaked in the test brine for about a week to establish ionic equilibrium. Plates were immersed in fresh test brine, and the brine phase was covered with a layer of crude oil. In the second procedure, after the initial soaking, the plates were drained, but not dried, and then submerged in crude oil for an aging time, t_a, at an aging temperature T_a. After aging, excess crude oil was removed from the plate by rinsing with toluene using the method described by Liu and Buckley (1997). Toluene was removed by air drying. Contact angles, determined by dynamic Wilhelmy plate method, were measured at temperature T_m. The plate was first immersed in the test brine, which was then covered with a layer of clean decane. Details of the experimental procedures are available (Xie, 1996).

RESULTS AND DISCUSSION

Brine pH. Adhesion maps for many crude oils show adhesion at low pH and non-adhesion at high pH (Buckley and Morrow, 1990). These transitions in wettability have been modeled mathematically as sharp transitions from strongly water-wet to strongly oil-wet (Kovscek *et al*., 1993). Measurement of change in contact angle with pH provides a more detailed account of change in wettability with pH exhibited by crude oil. With decane, θ_R and θ_A were zero for all values of pH (Xie, 1996). Contact angles measured with clean plates (see **Fig. 1**) for CS and A'95 crude oils are shown in **Fig. 2.** NaCl brines ranging in pH from 4 to 10 and molarity from 0.01 to 1 were tested. For A'95 crude oil at low brine pH, advancing contact angles were high with the most dilute brine giving the highest angles. As the brine pH increased to 7 or 8, most advancing angles decreased to 35° or less. The effect of pH on interfacial tension (IFT) may also be significant. IFT vs. pH is included in **Fig. 2** for the same range of pH and salinity. Sensitivity of IFT to ionic strength was highest for CS crude oil at pH = 10.

Receding contact angles were consistently low (all less than 45°), and relatively insensitive to both pH and salinity over the range of investigation. Both crude oils showed minimum advancing and receding angles and maximum IFTs at neutral pH, with that for CS oil being particularly well identified. For purified decane/brine systems, interfacial tensions were much higher than for crude oils (**Fig. 2**).

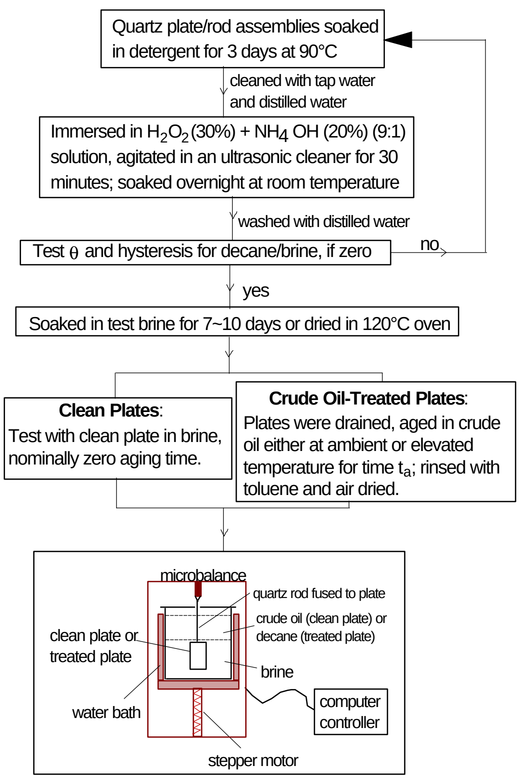

Fig. 1 Alteration of the wettability of quartz plates by adsorption from crude oil.

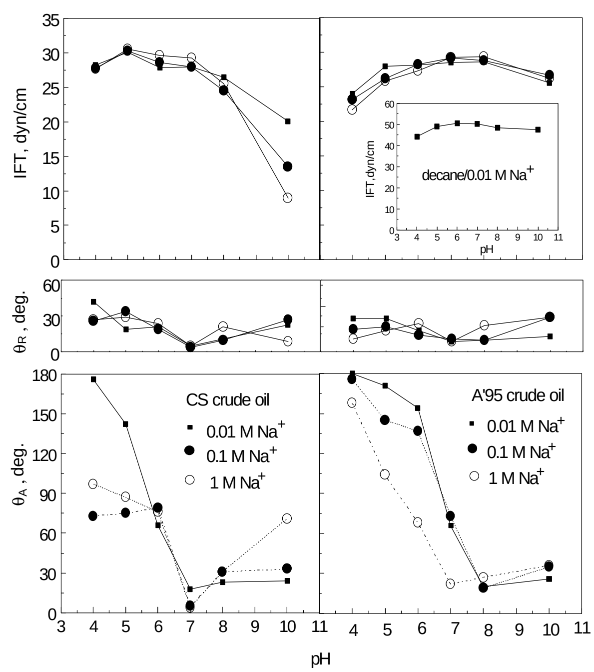

Fig. 2 The effect of pH and concentration of NaCl brine on initially clean plates submerged in brine prior to contact with crude oil (clean plate procedure, Fig.1).

Aging time t_a and aging temperature T_a. For oil-treated plates aged at room temperature for times ranging from 1 to 500 hours, neither A'93 nor CS crude oil promoted contact angles with PB brine of above 60° (**Fig. 3**). Contact angles for CS crude oil increased from 30° to about 60° during the first 72 hours of aging, but were only about 30° for aging times ranging from 144 to 504 hours. The behavior of plates contacted with A'93 crude oil showed a similar trend with final contact angles being close to 40°. All of the plates treated at ambient temperature remained water-wet.

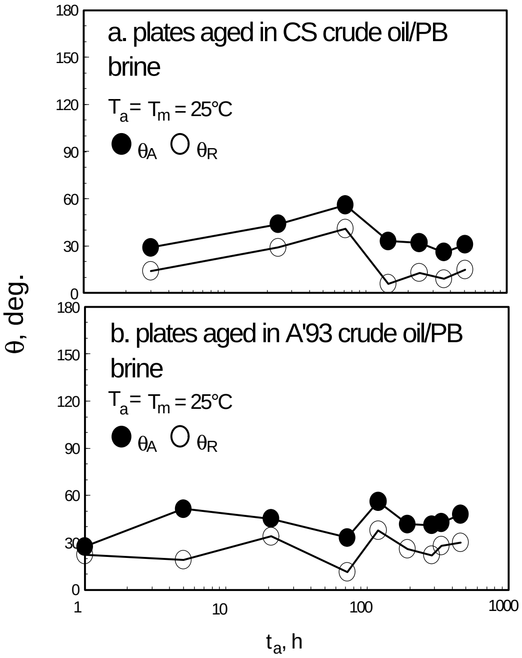

Fig. 3 Contact angles for decane/PB brine/treated plates aged at room temperature.

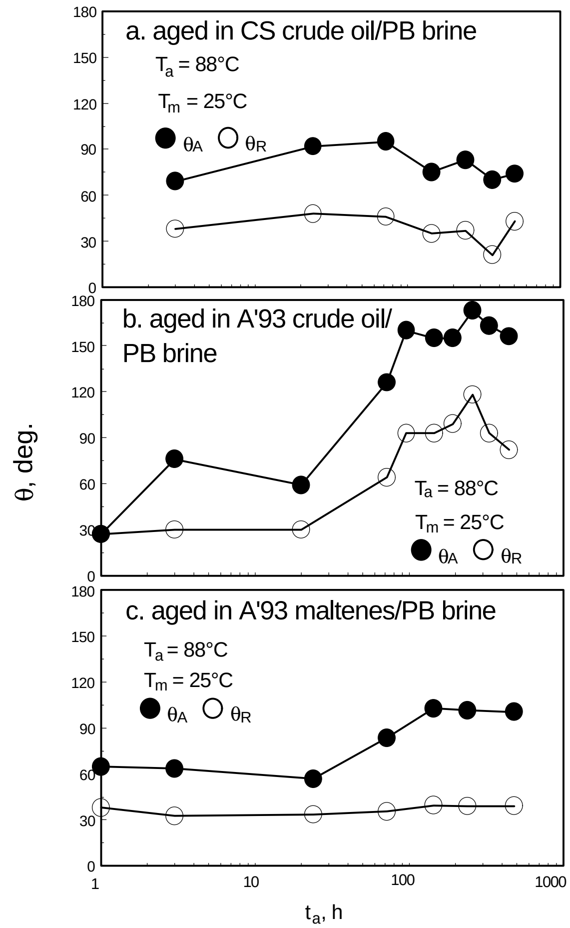

Fig. 4 Contact angles for decane/PB brine/treated plates aged at high temperature.

At T_a = 88°C, aging of plates in crude oil resulted in marked increase in contact angles for both crude oils relative to those observed after aging at room temperature (*cf.* **Figs. 3, 4a,** and **4b**). For CS crude oil, advancing angles again increased (from 69° to 95°) with t_a up to 72 hours but fell to about 75 ± 8° with further aging. Contact angles on plates aged in A'93 crude oil increased with aging times of up to 96 hours. For 96 hour aging, θ_A was 150°. Above 96 hours aging, the advancing angles were all in the range of 150 to 170°; receding angles were all much lower but showed comparable trends.

Oil composition. The wetting properties of the rock can be altered from strongly water-wet by adsorption of polar compounds, often identified as asphaltenes, from the crude oil. Results for de-asphalted A'93 crude oil (heptane maltenes) are shown in **Fig. 4c**. Change in wettability induced by the maltenes was, as expected, less than that for the parent crude oil (*cf*. **Figs. 4b** and **4c**) but still comparable to the changes for CS crude oil (*cf*. **Figs. 4a** and **4c**). The differences, observed for different oils with the same brine, underscore the importance of crude oil composition in wetting alteration.

Temperature of measurement T_m. Results for treated plates are shown for three synthetic reservoir brines (RB), designated as CS, DG and PB. Diluted brines, with total dissolved solids of reservoir brine reduced to one-tenth and one-hundredth, were designated as 0.1RB and 0.01RB. All of the advancing contact angles measured at reservoir temperature were lower than those measured at room temperature (**Fig. 5**). This result is consistent with the adhesion tests reported by Buckley *et al*. (1996b). The receding angles measured at both room and reservoir temperature were all low (see **Table 3**).

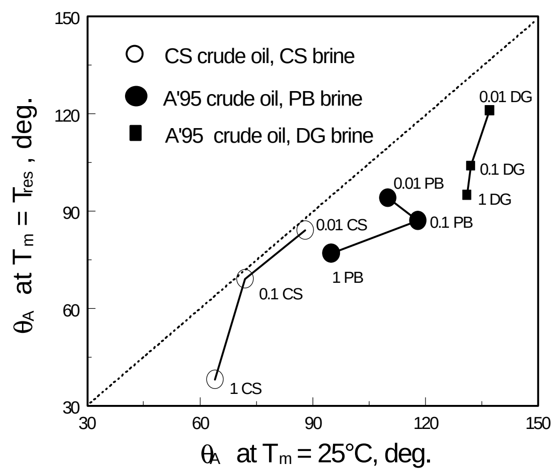

Fig. 5 The effect of temperature of measurement on advancing angles.

Table 3. Receding angles (deg.) corresponding to advancing angles shown in **Fig. 5**

Brine	0.01CS	0.1CS	CS	0.01DG	0.1DG	DG	0.01PB	0.1PB	PB
T_m = 25°C.	37	28	31	32	39	55	49	42	43
$T_m = T_{res.}$	35	29	15	24	49	40	30	33	37

Brine composition. Imbibition and waterflood tests have been reported for synthetic reservoir brines and for dilutions to one-tenth and one-hundredth of their original concentrations (Tang and Morrow, 1996). The advancing contact angle measurements shown in **Fig. 5** are presented in **Fig. 6** as plots of contact angle vs brine composition. Dilution of the brine resulted in increased advancing contact angles for all of the high temperature tests. The same trend was observed at low temperature for CS and DG brines.

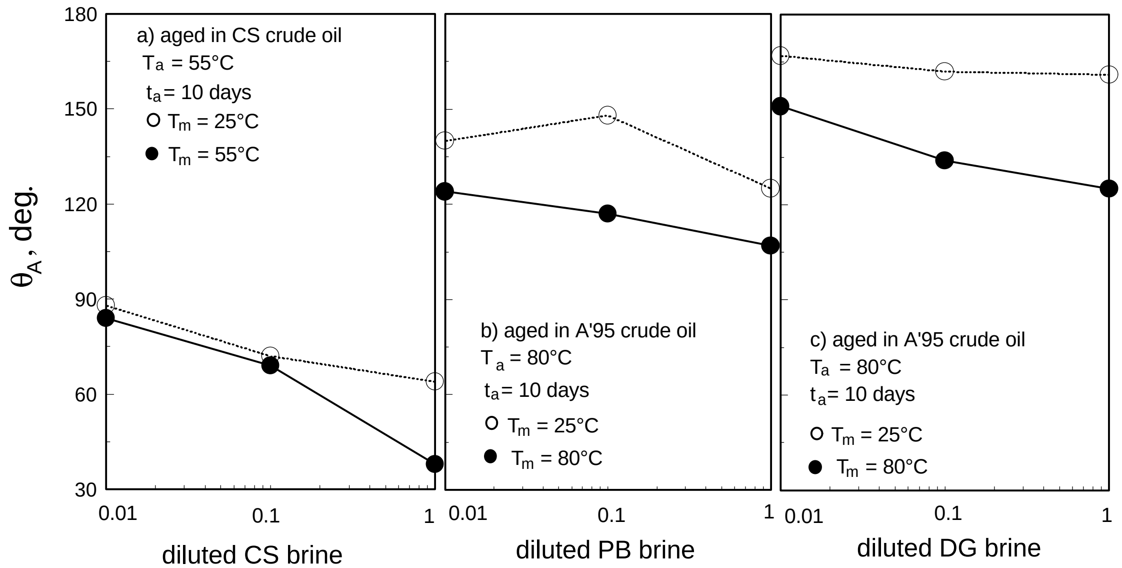

Fig. 6 The effect of brine composition on advancing contact angles.

Contact angles and oil recovery from cores. The contact angles measured on flat quartz surfaces permit comparison with previously reported information on the wettability of porous media as indicated by spontaneous imbibition and waterflood recovery.

Influence of brine pH: The dramatic change in contact angle and adhesion behavior with pH (see **Fig. 2**) suggests that pH control may provide a useful approach to predictably changing the wettability of crude oil/brine/rock ensembles. However, brine-rock interactions often change the pH of the injected brine. For Aerolith, a synthetic siliceous porous media, the pH of produced brine was equal to that of the injected brine. Imbibition tests for these core plugs showed very high imbibition rates for pH 8 brine and very slow imbibition for pH 4 brine (**Fig. 7**).

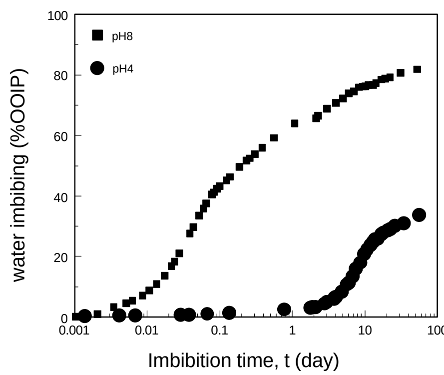

Fig. 7 Imbibition of water into Aerolith-10 after aging in A'93 crude oil (after Buckley *et al.*, 1996a).

Effect of aging time: Recovery of A'93 crude oil by spontaneous imbibition vs. dimensionless time is shown in **Fig. 8** for nominal initial water saturations (S_{wi}) of 15% and 20% (Wang, 1996) and aging at 88°C for times ranging from 4 to 240 hours (Zhou *et al.*, 1995). Comparison of recovery of refined oil (also shown in **Fig. 8**) and crude oil by imbibition for different S_{wi} demonstrates the marked change in wettability caused by exposure of the rock to A'93 crude oil. Lower S_{wi} results in lower imbibition rates and recovery. However aging time, for the range studied, clearly has a dominant effect on imbibition. Trends of increase in contact angles with aging time are in qualitative agreement with decrease in imbibition rate with aging time.

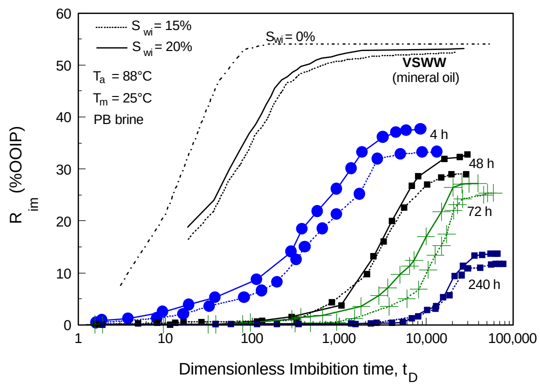

Fig. 8 Imbibition curves for Berea sandstone cores aged in A'93 crude oil at 88°C for different aging times.

Brine salinity effects: Recent results showed that dilution of brine can result in increased waterflood recoveries (Tang and Morrow, 1996). Imbibition and waterflooding tests with CS brine showed a consistent trend: the more dilute the brine, the higher the oil recoveries by both spontaneous imbibition and waterflooding (**Fig. 9**). Early time imbibition results for the three brine compositions were very close to each other and to correlated results for very strongly water-wet conditions; any differences in wetting states for the three brines cannot be determined from the imbibition rates. An index, I'_w, similar to the Amott index to water (Amott, 1959), can be defined as the ratio of oil recovery by spontaneous imbibition to oil recovery by forced displacement from two separate experiments (Zhou *et al*., 1996). For the results shown in **Fig. 9**, the values of I'_w for displacements with CS, 0.1 CS and 0.01 CS brines are 0.8, 0.81 and 0.90, respectively. This suggests some slight increase in water-wetness with brine dilution. However, other factors suggest the possibility of an opposite trend. Modest increases in contact angle have been shown to inhibit snap-off and can thus result in increased displacement efficiency (Li and Wardlaw, 1986). A maximum in imbibition recovery with decrease in water wetness has been ascribed to this mechanism (Ma *et al*., 1994). The marked increase in contact angle at $T_m = T_{res}$ with decrease in brine concentration shown in **Fig. 6a**, also indicates that water-wetness decreases with brine dilution. Increase in oil recovery with decrease in water wetness is consistent with previous observations

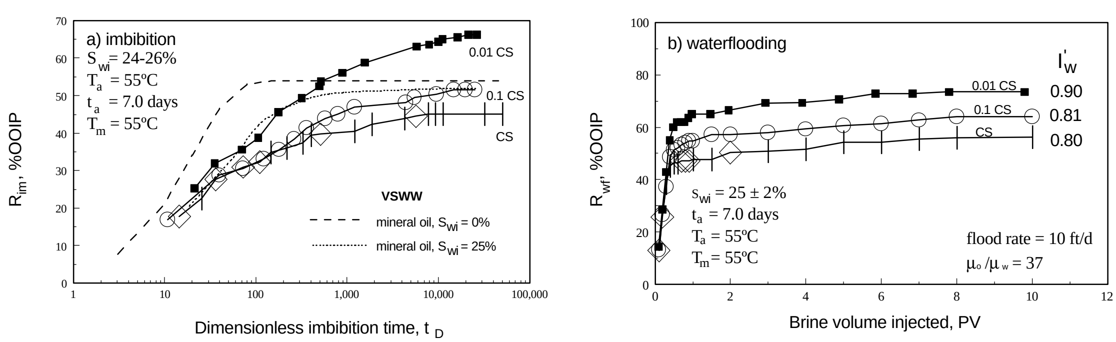

Fig. 9 The effect of brine concentration on recovery of CS crude oil by imbibition and waterflooding from Berea sandstone (Morrow, *et al*., 1996).

(Jadhunandan and Morrow, 1995) and with the predictions of network models assuming ranges of contact angles (Dixit *et al*., 1996). Thus, large differences in oil recovery can occur in situations where the underlying effect of oil/brine/rock interactions is not obvious.

Contact angles and imbibition: Relationships between displacement behavior and contact angle were studied using cores formed from consolidated polytetraflueroethylene (PTFE) powders and pure liquids vs air (Morrow and McCaffery, 1978). Spontaneous imbibition measurements showed that with an initial liquid saturation in PTFE cores, liquids with equilibrium contact angles at flat surfaces greater than about 62° did not imbibe. Thus, if contact angles measured at quartz surfaces (see **Fig. 4b**) are relevant to the wetting behavior of Berea sandstone, the displacement of oil by spontaneous imbibition is surprising, particularly for low pH brine (*cf*. **Figs. 2** and **7**) and for the long aging times (above 100 hours) that give advancing contact angles in the 150-180° range (*cf*. **Figs. 4b** and **8**).

Although, for PTFE surfaces, roughness could result in even higher contact angles (Morrow, 1975), it is probably reasonable to regard the advancing angles measured for crude oil and brine as limiting values. Ma *et al*. (1996) calculated that water held in the corners of triangular pores at the drainage curvature, with $\theta_R = 0°$, can promote spontaneous imbibition even when advancing contact angles at the drained surfaces of the tubes are as high as 130°. Water retained by fine pores and surface asperities as well as wetting of minerals that are more water-wet than quartz may also promote imbibition.

Achievement of the positive oil-brine interface curvature necessary for imbibition in porous media may sometimes also involve slow decrease in contact angles with time. This would explain the induction time required before imbibition commences and very slow rates of imbibition, as shown in **Fig. 8** (see discussion by Zhou *et al*., 1996). Liu and Buckley (1997) showed decreasing contact angles on oil-treated surfaces soaked in brine. Change towards water-wet conditions was reported by Tang and Morrow (1996) for Berea sandstone cores aged at waterflood residual oil saturation. This shift in wetting is consistent with reports of more water-wet conditions in reservoir cores after waterflooding (Jin *et al*., 1985).

CONCLUSIONS

1. The Wilhelmy plate technique is a convenient method of characterizing the wettability of oil/water/solid systems through measurement of contact angles under dynamic conditions.

2. Wettability changes on quartz surfaces induced by crude oil are strongly dependent on crude oil composition. The wettability of an oil/brine/quartz system also depends on surface pretreatment, the brine composition and pH.

3. Aging temperature is demonstrated to be a very important factor in wetting alteration. Quartz surfaces aged with crude oil at room temperature exhibited wettability change, but all remained water-wet. For aging at elevated temperature, water-wet quartz becomes intermediately wet or strongly oil-wet, depending on the crude oil composition.

4. Contact angles measured at reservoir temperature increased with decrease in brine concentration.

5. The wetting and recovery behavior of mineralogically and geometrically complex sandstones and an artificial siliceous media showed trends that could be related to contact angle measurements at smooth surfaces. For all these trends, porous media appear to be generally more water-wet, as evidenced by spontaneous imbibition, than indicated by contact angle measurements at flat quartz surfaces.

6. Wettability states induced by adsorption of crude oil components sometimes appear to revert towards water-wetness.

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