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Some mechanisms of crude oil/brine/solid interactions

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Abstract

Mechanisms by which crude oil components may adsorb on high energy mineral surfaces include polar, acid/base, and ion-binding interactions. Surface precipitation of asphaltic material can further alter surface wetting. Design of controlled experiments to investigate the contributions of different mechanisms is hindered by the lack of simple, well-characterized analogs for crude oils that show even qualitatively similar interfacial properties. As an alternative, we observe the wettability altering tendencies of a variety of crude oils with the aim of relating the fluid/solid interactions to crude oil composition. The mixtures of compounds in crude oils, variability of samples, and changes that can occur during storage, all add to the uncertainties of mechanistic studies with crude oils. Nevertheless, consistent trends can be identified. © 1998 Published by Elsevier Science B.V. All rights reserved.

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1. Mechanisms of interaction

The main categories of crude oil/brine/solid (COBS) interactions identified thus far include:

- *polar* interactions that predominate in the absence of a water film between oil and solid,
- *surface precipitation*, dependent mainly on crude oil solvent properties with respect to the asphaltenes,
- *acid / base* interactions that control surface charge at oil/water and solid/water interfaces, and
- *ion-binding* or specific interactions between charged sites and higher valency ions.

Distinctions between mechanisms of interaction are most readily apparent using the smooth surface techniques, described in detail previously (Buckley et al., 1989; Buckley and Morrow, 1991; Liu and Buckley, 1997). Smooth surfaces of glass or mineral are cleaned, equilibrated with the aqueous phase, drained briefly (or dried), then aged in crude oil. Variables include oil and brine compositions, aging time and aging temperature. After aging, crude oil is removed by rinsing—usually with toluene—and contact angles between decane and water are measured.

1.1. Polar interactions

Clean, dry surfaces have been aged in a variety of crude oils and their asphaltene fractions. Under these conditions, interactions that alter surface wetting can occur between polar functional groups in the oil and polar surface sites. The advancing angles (θ_A) measured with decane and water are intermediate and the

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extent of interaction changes little with either aging time or aging temperature.

1.2. Surface precipitation

Crude oils vary in their ability to solvate their asphaltenes. Some indicators of poor solvent quality are low refractive index or high API gravity (low density). If the oil is a poor solvent for the asphaltenes, the tendency for wetting alteration is enhanced (Buckley et al., 1997). The effect of precipitation is readily illustrated if, after aging in crude oil, surfaces are washed with decane instead of toluene. Because decane induces asphaltene precipitation, the surface immediately becomes oil-wet. Receding angles (θ_R) are high and hysteresis between θ_A and θ_R is small.

1.3. Acid / base interactions

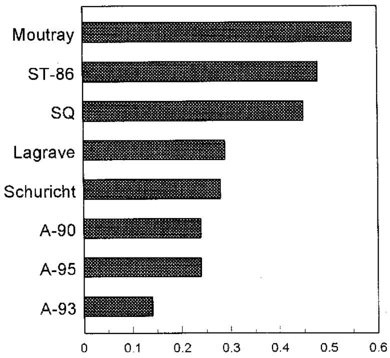
Water plays an important role in mediating oil/solid interactions. In the presence of water, both the solid and oil interfaces become charged. Polar functional groups belonging to both the mineral and crude oil phases can behave as acids (giving up a proton and becoming negatively charged) and bases (gaining a proton and a positive charge) (Cuiec, 1975). There are two major ways in which the phenomenon of surface charge impacts COBS interactions.

(1) *Net charge affects water film stability.* The influence of DLVO forces in stabilizing a thin film of water between mineral and oil is most significant when the brine phase salinity is low and composed of monovalent ions. Under these conditions, the main variable influencing surface charge and thus water film stability is pH, since the acid/base equilibria and thus the extent of surface charge are all governed by pH.

(2) *Ionized acidic and / or basic sites influence adsorption.* Collapse of the water film is only the first step in wetting alteration. At this stage, crude oil components at the oil/brine interface can adsorb on the solid surface. Silica surfaces are negatively charged above pH 2; positively charged nitrogen bases can adsorb (Anderson, 1986). Calcite surfaces are positively charged below a pH of about 9.5; acidic species adsorb (Morrow et al., 1973; Thomas et al., 1993).

There is considerable diversity between crude oils in the extent to which they alter wetting by acid/base interactions. Acid and base numbers of a selection of crude oils are shown in Fig. 1. Interactions with a silica surface by the acid/base mechanism should be maximized with an oil such as A-93 which has high base and low acid numbers. A-93 can produce very high water advancing angles on borosilicate glass surfaces (Liu and Buckley, 1997; Buckley et al., 1996). If a glass surface is equilibrated with a pH 4, 0.1 M NaCl solution and aged in oil at 80°C, θ_A is finite for measurements after a few hours of aging. After 7 days of aging in this oil, the residual θ_A has increased to 142° and the hysteresis between advancing and receding conditions is dramatic. If the pH is raised and the same procedure is followed, much more water-wet conditions can be maintained with the same oil ($\theta_A = 30°$ after 5 days).

(a) Acid numbers



(b) Base numbers

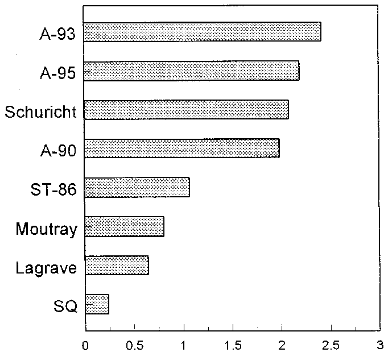


Fig. 1. Acid and base numbers, measured by nonaqueous potentiometric titration for selected crude oils (after Buckley et al., 1998).

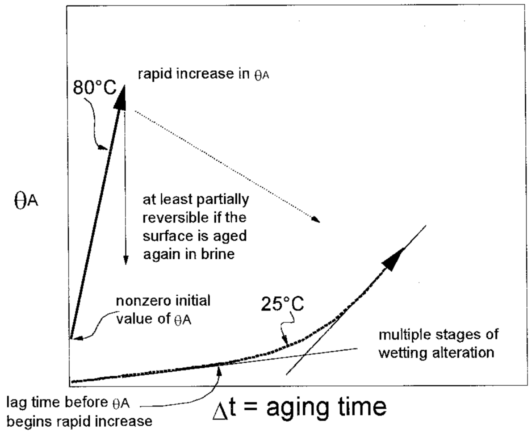


Fig. 2. Notation used to summarize characteristics of different interaction mechanisms in Table 1.

1.4. Ion-binding interactions

When present, Ca^{2+} ions mask the purely acid/base interactions. Several interactions are possible:

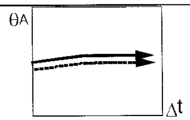
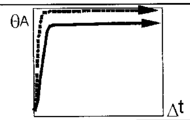
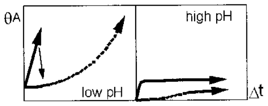
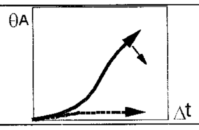
oil–Ca–oil mineral–Ca–mineral oil–Ca–mineral.

The first two can limit wettability alteration while the last promotes it. pH is no longer the major determining factor in adhesion experiments (Buckley and Morrow, 1991), neither is adhesion a good indicator of interactions that occur with longer exposure times. Longer exposure adsorption tests show that strong interactions can occur, but the interactions are very dependent on temperature (Liu and Buckley, 1997). High hysteresis, similar to that observed for acid/base interactions, has been observed. Interactions via ion binding appear to be somewhat more resistant to desorption than acid/base interactions.

1.5. Summary of COBS interaction mechanisms

Some of the characteristics identified for the four major categories of interaction are illustrated graphically in Fig. 2. The larger arrows indicate the rates at which decane/water contact angles typically increase on surfaces aged in oil. Solid lines indicate elevated temperature and dotted lines are for room conditions. Lighter, downward pointing arrows indicate the rate of desorption, where that has been tested (see Table 1).

Table 1
Mechanisms of interaction between crude oils, brine, and solid surfaces (after Buckley et al., 1998)

Type	Description	θ_A	hysteresis (θ_A - θ_R)	Effects of aging conditions
Polar	If there is no water present, the strongest interactions are between polar atoms (N,S,O) and polar surface sites.	~90°	moderate	
Surface precip-itation	Occurs when oil is a poor solvent for its asphaltenes. Changes in T, P, and in oil composition affect solvent properties.	~180°	low	
Acid/ base	Coulombic interactions between ionized acidic and basic sites. For **monovalent salt solutions at low concentration**, pH is the dominant variable.	depends on oil & brine	high	
Ion binding	Coulombic interactions. Divalent and multivalent ions can bind at both oil and solid/water interfaces and/or bridge between them.	depends on oil & brine	high	

2. Consequences of interaction mechanisms in sandstone cores

It is likely that more than one mechanism of interaction contributes to crude oil/brine/rock (COBR) interactions. Nevertheless, by comparing acidic and basic oils, and oils of varying solvent quality, it is possible to see differences in wetting alteration that are consistent with the outlined mechanisms. Polar interactions between oil and dry surfaces are likely to be less significant in cores where water is always the first fluid occupying the pore space.

2.1. Surface precipitation

The best known example of wettability alteration by destabilizing the asphaltenes in a crude oil is the work of Salathiel (1973). In order to induce wettability alteration in cores, the crude oil was diluted with *n*-heptane. It is likely that surface precipitation contributed to the mixed-wet conditions observed.

Another good example is Lagrave crude oil. Lagrave readily alters wetting on silica and in sandstone cores (Morrow et al., 1994), despite having only an intermediate acid number and low base number. The laboratory sample has a high API gravity (41°) and contains asphaltene precipitate without addition of precipitating agent.

2.2. Acid / base interactions

The effect of aging Aerolith-10, a synthetic porous medium that is primarily silica, in A-93 crude oil has been shown to vary depending on brine pH (Buckley et al., 1996). Low pH, favoring positive charge of basic functional groups, produced weakly water-wet conditions ($I_w = 0.5$), whereas at higher pH, with the

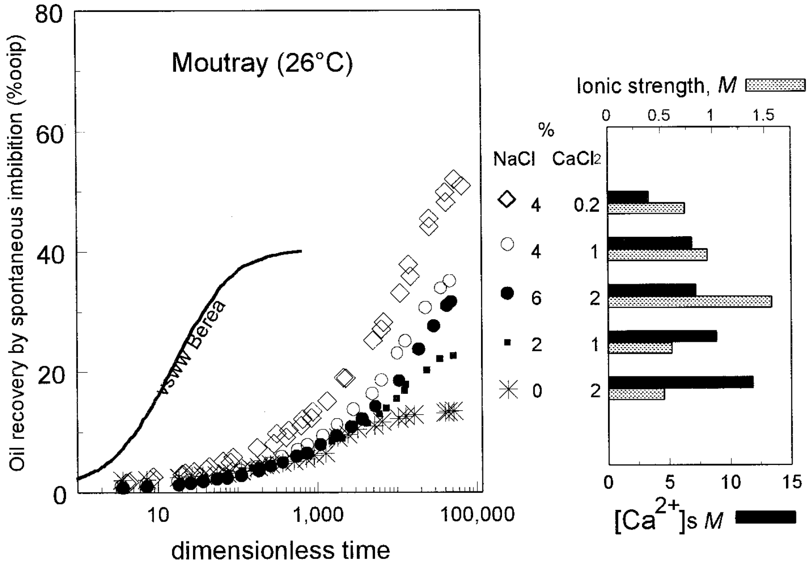


Fig. 3. Imbibition into Berea sandstone cores aged first in brine, then in Moutray crude oil for 10 days at 26°C (Jadhunandan, 1990). Dimensionless time is defined as:

$$t_D = t\sqrt{\frac{k}{\phi}}\frac{\sigma}{\sqrt{\mu_o\,\mu_w}}\frac{1}{L_c},$$

where t is time, k is permeability, ϕ is porosity, σ is interfacial tension, μ_o and μ_w are the viscosities of oil and water, and L_c is a characteristic length (Zhang et al., 1995). $[Ca^{2+}]_s$ is calculated from the Graham equation (Israelachvili, 1991) for a surface charge of -0.2 C/m^2 (after Buckley et al., 1998).

Table 2
G-AB parameters for four crude oils

Crude oil	G API	Acid # (mg KOH/g oil)	Base # (mg KOH/g oil)
A-93	26	0.1	2.4
Lagrave	41	0.3	0.7
Moutray	35	0.6	0.8
ST-86	28	0.5	1.1

same crude oil and aging conditions, strongly water-wet conditions ($I_w = 1$) were maintained.

2.3. Ion binding—three crude oils in Berea sandstone

In natural sandstones, the interactions are more complex than in Aerolith. Acid/base interactions may still be important, but they cannot readily be isolated from the more complex contributions of the ion-binding mechanism (Denekas et al., 1959; Cuiec, 1975; Buckley et al., 1996). Ion binding provides an alternative mechanism for wetting alteration by which ions of the same sign as the solid surface can contribute. The details of this binding mechanism are undoubtedly complex and have yet to be worked out, but its consequences can be observed.

Fig. 3 shows that wetting of Berea sandstone cores varies with the composition of the brine phase for cores aged at 26°C (Jadhunandan, 1990). The trend does not correlate, however, with either $[Ca^{2+}]$ or ionic strength. When the experiment was repeated with aging at 80°C, the imbibition rates all fell between the lower two curves. Evidently, 10 days is not sufficient aging time to reach equilibrium at room temperature.

Counter ions (Na^+ and Ca^{2+}) are concentrated in the double layer near a negatively charged surface. At high salinities, the calculated values of calcium ions at the negatively charged solid surface ($[Ca^{2+}]_s$), as shown in the bar graph in Fig. 3, likely give only relative comparisons between these brines. The rate of imbibition decreases systematically with these calculated values of $[Ca^{2+}]_s$, suggesting that calcium ions are specifically involved in the interaction mechanism. Moutray, with a high acid number (Fig. 1a), has many negatively charged interfacial sites and depends on the ion-binding mechanism for its wettability-altering behavior.

Less acidic crude oils and those with different interfacial ratios of bases to acids respond differently than Moutray to changes in calcium ion concentration in the brine. For A-92, probably a fairly basic oil (judging by the other samples tested from the same reservoir: A-90, A-93, and A-95), increasing $[Ca^{2+}]_s$, *increases* the amount of oil produced by spontaneous imbibition (Yildiz, 1995). Wetting alteration by ST-86 (intermediate acid and base numbers and similar numbers of acids and bases at the oil/water interface) (Buckley et al., 1989) is almost completely insensitive to brine composition (Jadhunandan, 1990).

3. Crude oil composition and wettability alteration—the G-AB profile

Since there are several distinct mechanisms by which a crude oil can alter wetting, oil compositional characteristics are needed that relate directly to these mechanisms. To a first approximation, oils can be evaluated using three properties, as shown in Table 2. These are API *gravity* (a measure of solvent quality of the oil), *acid* and *base* numbers. Together these three properties, the G-AB parameters of the

Table 3
G-AB profile for evaluation of potential wetting alteration by a crude oil

Mechanism	Oil property	Example	Rock	Wetting alteration enhanced by
Surface precipitation	API gravity (G)	Lagrave		high API = low density = poor solvent quality
Acid/base	acid and base # (AB)	A-93	ss	high base # + low acid #
			cb	low base # + high acid #
Ion binding	acid and base # (AB)	Moutray	ss	high acid #
			cb	high base #

ss = sandstone, cb = carbonate.

oil, can be used to evaluate the potential for a particular crude oil to alter wetting.

Note that none of these parameters alone is particularly significant. Rather, it is in combination that they can give a qualitative indication of the extent to which an oil, in a particular suite of COBR variables, will alter wetting. A-93, for example, does not only have a high base number, it also has a very low acid number. Together, these characteristics promote acid/base interactions in sandstones. Lagrave, with smaller amounts of both acids and bases than most of the other oils in Table 2, still alters wetting significantly (Morrow et al., 1994), as predicted by its very high gravity. Application of G-AB profiles is summarized in Table 3.

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