

Mechanisms and Consequences of Wettability Alteration by Crude Oils

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Symbols and Abbreviations

A	area (cm ²)	I	wettability indices
AFM	atomic forces microscopy	I _o	Amott index to oil
A ⁻	dissociated organic acid	I _w	Amott index to water
AH	protonated organic acid	I _{w-o}	Amott-Harvey index
BH	dissociated organic base	I _{USBM}	USBM wettability index
BH ₂ ⁺	protonated organic base	IEP	isoelectric point
BT Rec	breakthrough waterflood recovery (%OOIP)	IFT	interfacial tension
C	curvature	ISG	ionizable site group
C _i	concentration of species i (moles/L)	k	Boltzmann constant
COBR	crude oil/brine/rock	k _r	relative permeability
cot φ	indicator of solvent power (Fig. 2-14)	K	permeability (md)
CSC	critical salt concentration	K _{N₂}	permeability to nitrogen (md)
DLVO	Derjaguin-Landau-Verwey-Overbeek	K _{brine}	permeability to brine (md)
e	- charge on an electron (C)	K _{o(Swi)}	permeability to oil at S _{wi} (md)
F	force (N)	K _a , K ₊ , K ₋	equilibrium constants
F _b	buoyancy force	L	length (cm)
F _i	interfacial force	L _c	critical length for scaling rate of imbibition
FR	flocculation ratio	M	molecular weight
f _v	volume fraction	N _a	number of ionizable sites (or number of acidic sites)
f _{v, oil}	volume fraction of oil	N _b	number of basic ionizable sites
f _{v, ppt}	volume fraction of precipitant	n _D ²⁰	refractive index measured with the sodium D line at 20°C
g	acceleration due to gravity	N _o	Avogadro's number
G-AB	API gravity-acid # and base #	OOIP	original oil in place
h	height (cm)	P _c	capillary pressure
		P	perimeter

P	polarization	T	titrant volume (Fig. 2-14)
P_d	distortion polarization	T_o	volume of titrant at onset of imbibition (Fig. 2-14)
P_M	molar polarization	V	volume
P_μ	orientation polarization	V_p	volume of precipitant
pH	$-\log [H^+]$	V_s	volume of solvent
pK _a	$-\log K_a$	V_{front}	frontal velocity (ft/day)
P_{RI}	refractive index at the onset of asphaltene pptn.	vsww	very strongly water-wet
P_{RI}^*	estimated refractive index at onset of asphaltene pptn.	X	mole fraction
PV	pore volumes	y_o	reduced potential $y_o = e\psi_o/kT$
PVI	pore volumes injected	z	valence
r_1, r_2	radii of curvature	α	fraction of oil-filled pores that are oil-wet
R_M	molar refraction	α_{Cr}	percolation threshold
RI	refractive index	γ	interfacial tension (dyn/cm)
RO	refined oil	γ_{os}	oil-solid IFT
S	solvent volume (Fig. 2-14)	γ_{ow}	oil-water IFT
S	saturation (PV)	γ_{ws}	water-solid IFT
S_{or}	remaining oil saturation	δ	solubility parameter (cal/ml) ^{1/2}
S_{wi}	initial water saturation	θ	contact angle measured through aqueous phase (degrees)
$\Delta S_{w,imb}$	change in water saturation by spontaneous imbibition	θ_A	water advancing contact angle
$\Delta S_{w,total}$	total change in water saturation by imbibition and waterflood	θ_R	water receding contact angle
SANS	small angle neutron scattering	μ	viscosity (cp)
SAXS	small angle X-ray scattering	μ_o	viscosity of oil
SVPO	180-190 Saybolt viscosity paraffin oil	μ_w	viscosity of water
t	time	ρ	density (g/cm ³)
t_a	aging time in oil	ρ	number density of molecular species (molecules/m ³)
t_D	scaled time of imbibition	σ_o	surface charge (C/m ²)
T	temperature (°C, or K)	ψ_o	surface potential (V)
T_a	temperature during aging in oil		

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Abstract

Reservoir wettability is controlled by crude oil/brine/rock interactions that have not been well understood. Studies using either model compounds or crude oil fractions have had only limited success in reproducing the wetting alteration that can occur in nature. In this study, the approach is first to identify the key features of interfacial activity unique to crude oils, then to design and conduct wetting alteration experiments—using both flat solids and porous media—that demonstrate the mechanisms by which alteration can occur.

Components of crude oils that are interfacially active are found in the highest molecular weight, most polar fractions of the oil, the resins and asphaltenes. How these components affect wetting depends on the compositions of not only the oil, but also the mineral surfaces and the aqueous phase that is always present in oil reservoirs.

Wettability altering interactions can occur by several mechanisms. In the absence of water, adsorption of polar species can create intermediately-wet surfaces. If the oil is a poor solvent for its asphaltene fraction, adsorption of large asphaltene aggregates can make surfaces fairly oil-wet. Adsorption can also occur because of ionic interactions between oppositely charged acidic and basic sites at the oil/water and solid/water interfaces. There may also be interactions between similarly charged sites, if ion binding can occur. All of these mechanisms have been documented for a range of crude oils with varying asphaltene fraction, solvency, acid number, and base number.

Introduction

Oil recovery efficiency is strongly influenced by capillary forces at the pore scale. The magnitude of those capillary forces depends on the curvature of oil/water interfaces confined within the porous, oil-containing rock. Pore geometry and surface energetics or wettability are the factors that together determine shapes that these interfaces must assume during a displacement process, such as a waterflood. The focus of this thesis is on understanding the wide range of wettability conditions that can exist in an oil reservoir, why they occur and how they affect oil recovery. It is principally a *mechanistic* study of the underlying chemistry that controls wettability in real fluid/rock systems.

Wettability is precisely defined only in the context of two pure fluids contacting a molecularly smooth solid. Oil reservoirs obviously do not meet these criteria. The challenge is to discover which of the many complexities in oil reservoirs significantly impact surface wettability conditions.

It is generally agreed that water (or brine) is the first fluid to occupy the pore space and that most of the reservoir minerals have high energy surfaces and are initially water-wet. It is also known that crude oils contain components with polar functionality that can be interfacially active. There are not, however, obvious relationships between either the composition or amount of the polar components that correlate with wettability as determined by any of the empirical methods currently used to assess wettability of porous media. Why one oil has more effect on wetting than another has long been a puzzle. Many pieces of this puzzle have been recognized, but there has been less progress in fitting the pieces together.

Part of the difficulty may lie in the empirical methods themselves, as discussed in Chapter 1. A bigger problem, however, is the lack of a fundamental understanding of the varied and complex interactions that can occur in crude oil/brine/rock (COBR) ensembles. Is material adsorbed directly from the oil phase onto solid surfaces? How is this accomplished, given that water initially wets those surfaces? What materials adsorb, how strongly or reversibly, and how does temperature affect the process? Ideally these are questions that might be investigated using model systems. Unfortunately, no model compounds have yet been found that can reproduce COBR interactions. Crude oils, however complex and poorly characterized, are a necessary part of the study of oil reservoir wettability.

In this thesis, we begin by considering the crude oil. Components, especially those with the potential to be interfacially active, are reviewed in Chapter 2. Interactions between several crude oils and borosilicate glass surfaces in the absence of water are shown. These will be compared, in subsequent chapters, to the more realistic case where water is an important factor.

Interfacial activity of components in the oil phase is influenced by the solvent quality of the oil. A correlation of the refractive index of a mixture containing crude oil, various non-polar solvents, and precipitants with the onset of asphaltene precipitation is demonstrated in Chapter 2. This correlation provides the basis for a novel way to characterize the solvent quality of crude oils. Insofar as asphaltenes can be equated with the surface active material, refractive indices can provide valuable insight into the environment of the interfacially active species in a particular oil. The ability of the oil to act as a good or poor solvent for the interfacially active components is an important piece in the wettability puzzle.

The next level of complexity that must be considered is the interaction between crude oils and water. In Chapter 3, the oil/water interface is examined in detail. Measurements of interfacial tension and electrophoretic mobility lead to a picture of an oil/water interface that can best be described as zwitterionic (i.e. having both positively *and* negatively charged sites). The zwitterionic character of the crude oil/brine interface is a second key piece of the wettability puzzle. A third piece, the influence of brine composition on COBR interactions, follows from understanding that charged species, both acids and bases, can be interfacially active. Exactly which ionic species exist at an interface with a particular oil is a function of brine ionic composition and pH. These ionic species can interact strongly with solid surfaces. Therefore, the details of the interaction between a given crude oil and a solid surface can vary widely depending on the composition of the brine phase.

These interactions are examined most simply in this work by contacting a drop of crude oil with a brine-covered surface. The results of this simple test are difficult to quantify, but fall into two broad categories: adhesion and nonadhesion. More detailed information on COBR interactions are provided by tests of adsorption onto wet surfaces aged in crude oils, with temperature and aging time as variables. The results of aging in crude oil have mainly been quantified by measurements of contact angles between water and decane, after the bulk crude oil has been washed away. Atomic forces microscopy has also been used to observe the results of these adsorption experiments. A novel interpretation, integrating the

effects of solvent quality, zwitterionic character of the interface, and the influence of brine is presented in Chapter 3 to explain the various COBR interactions observed in these tests. Fitting these three pieces of the wettability puzzle together to explain COBR interactions on smooth surfaces is a major contribution of this work.

There is a considerable gap between contact angle measurements on smooth surfaces and the various indirect indicators of wettability in porous media. The study reported in Chapter 4 helps to bridge this gap. An oil sample from Prudhoe Bay and two brines that varied only in pH were selected, based on smooth surface tests, to maximize the difference in COBR interactions while minimizing other variables that can affect displacements (interfacial tension and viscosity ratio, for example). Four porous media of increasing complexity were tested including: a glass micromodel, a synthetic core, a clean (clay-free) sandstone, and Berea sandstone which has a significant clay content. In the case of the synthetic core, where the surface properties most closely corresponded to the smooth surface tests on glass, a clear differentiation between water-wet and weakly water-wet conditions was demonstrated for experiments that were identical except for the pH of the brine. The wetting differences clearly corresponded to the COBR interactions demonstrated on smooth surfaces. Results in sandstones were, not unexpectedly, more complex, but were still generally consistent with predictable COBR interactions. Studying the mechanisms of COBR interactions directly is an important advance over trying to infer them strictly from the often conflicting clues provided by displacements in cores.

An important result from this multifaceted study of COBR interactions is the identification of several distinct mechanisms of interaction.

- Polar components in the oil can adsorb directly onto solid surfaces in the absence of bulk water. This interaction is fast and depends little on temperature. Dry glass surfaces exposed to crude oil become neutral with respect to wetting by water and oil.
- Acid/base interactions can occur when water is present in thin films. These are more time and temperature dependent than the polar interactions.
- Divalent and multivalent ions can add to the range and sometimes to the strength of interactions. Ion-binding interactions can develop quite slowly.
- Surface precipitation can occur if the oil is not a good solvent for its asphaltenes.

The effect of a variable such as temperature is different for these different interaction mechanisms and can be predicted if a dominant mechanism can be identified. Commonly measured oil properties that can help explain which mechanisms are likely to be most

important for a given oil in combination with a particular rock type and brine composition are the acid and base numbers and the density (or gravity) of the oil. Less commonly measured, but probably a better indicator of solvent quality, is the refractive index of the oil and of oil/precipitant mixtures in which asphaltenes appear.

The mechanistic understanding of the interactions that can occur between crude oils, brine, and rock surfaces that has emerged from this study will help with the design of both surface and core tests in future so that more reliable predictions of reservoir wetting can be made from laboratory measurements. Control over these interaction mechanisms extends the possibility of improved studies in laboratory tests and even of improved oil recovery in the field.

Chapter 1

WETTABILITY AND ITS INFLUENCE ON OIL RECOVERY

Wettability is important in oil recovery processes in ways that are not always readily quantified. A variety of wetting conditions are likely, but detailed descriptions of actual wetting scenarios and the ways in which they can change during the productive life of an oil reservoir are not yet known. This chapter presents a brief review of wettability problems as they affect petroleum recovery and introduces the interactions between crude oils and mineral surfaces that will be the basis of this work.

Theoretical considerations of the flow of water and oil through sand or rocks often begin by assuming strongly water-wet conditions, which raises two immediate questions:

- How often are conditions strongly water-wet?
- How much difference does it make if they are not?

A growing body of evidence on the wetting of oil reservoirs indicates that strongly water-wet conditions are probably rare and that non-water-wet conditions can make very significant differences that are only partially accounted for by adjusting relative permeability curves in simulations. Some of the reasons why oil reservoir wettability is as yet only partially understood, despite years of active research, will be outlined in this introductory chapter. This will pave the way for taking a fresh look at the interactions between crude oils, brine, and rock surfaces in the remainder of this thesis.

Why is Wettability Important in Oil Recovery?

Surface forces, resulting from long-range interactions between molecules, are always present. Their relative importance—as compared, for example, to gravitational forces—depends in part on the dimensions of the areas of interfacial contact. Colloidal systems are loosely defined as those having at least one linear dimension in the range from nanometers to micrometers. Smaller systems generally fall in the realm of traditional chemistry, whereas larger ones are well-described by classical continuum physics. In the colloidal range, surface forces often play a dominant role.

Capillary rise in a cylindrical tube is a simple and familiar example of the transition between gravity and capillary dominated regimes. Inside a clean glass tube, water strongly wets the surface in preference to air. In a sufficiently small tube, that wetting preference translates into a perceptible elevation of the water level within the tube, as illustrated in Fig. 1-1. For a 10 μm radius tube, for example, the height of rise would

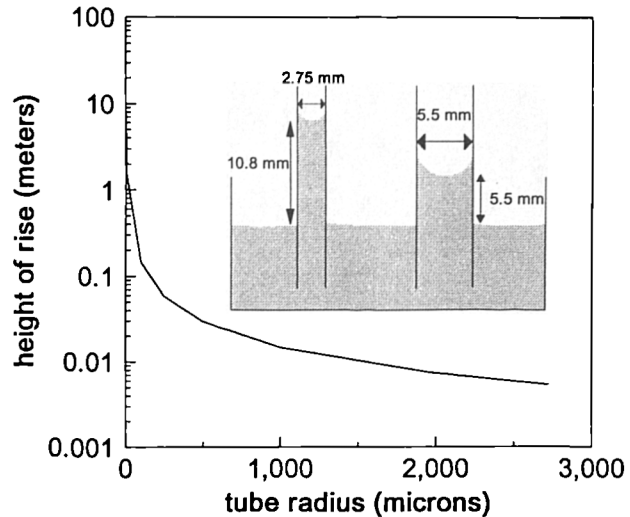


Figure 1-1 Capillary rise of water in a cylindrical tube calculated from $P_c = 2\gamma / r = \Delta\rho g h$ (assuming $\Delta\rho = 1 \text{ g/cm}^3$, $\gamma = 72.8 \text{ dyn/cm}$).

be on the order of 1.5 m, corresponding to a pressure difference across the interface of more than 2 psi.

It has long been recognized that oil is produced from micron-sized pores of reservoir rocks that are well within the colloidal size range. Since two or more immiscible fluid phases (water, oil, and gas) can coexist within the pore space, the influence of capillary forces must be considered. The magnitude of those forces is a function of the pore structure, the fluid properties, and the wetting conditions. The efficiency of any oil recovery process depends on the balance of capillary, viscous, and gravitational forces and whether each of these works for or against displacement of oil toward a producing well. Capillary forces are often the least predictable and readily quantified of the three.

A number of factors combine to make the capillary forces difficult to unravel:

- the pore space in a rock is geometrically and mineralogically complex,
- crude oils contain components that may adsorb on solid surfaces and alter wetting,
- there is no one direct measure of wetting in porous media, nor a satisfactory theoretical understanding of the measures that are commonly used, and
- the conditions under which crude oil components can adsorb and desorb are not well understood.

Defining and Measuring Wettability in Porous Media

In order to discuss wetting problems in oil recovery, it is necessary first to review the measures that are commonly used to assess wettability in porous media, their similarities and

their distinctions. Wettability reflects the relative affinities between a solid surface and two immiscible fluids. For pure compounds, there is a well-defined contact angle on homogeneous, smooth solid surfaces. This contact angle is a true thermodynamic quantity which can be derived either from minimizing free energy or a by force balance, as illustrated in Fig. 1-2a. Either approach yields the Young equation:

$$\gamma_{os} + \gamma_{ow} \cos(\pi - \theta) = \gamma_{ws}$$

where γ_{12} is the interfacial tension between phases 1 and 2. The phases in this illustration are oil, water, and solid, each indicated by its first letter in the subscripts.

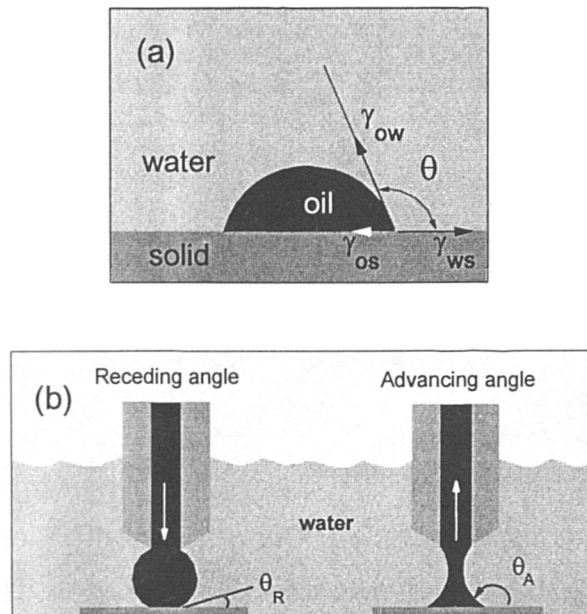


Figure 1-2. Contact angles: (a) convention for measurements and (b) contact angle hysteresis.

The conditions for measurement of this thermodynamic contact angle are never met in crude oil/brine/rock systems. The hysteresis observed for crude oils and brine on mineral surfaces is illustrated in Fig. 1-2b. In the interests of consistency and to avoid confusion in these highly non-ideal systems, water is taken as the reference phase, whether it is wetting or not. Thus contact angles refer to the angle measured through the water phase, advancing conditions refer to water advancing, and receding to water receding.

The convention of water as the reference phase can be extended to the terminology used to describe displacement of one phase by the other in porous media, but here there is additional opportunity for confusion because the displacement mechanisms depend on wetting. In this work imbibition, which may be spontaneous or forced, implies an increase in water saturation. Similarly, drainage means a decrease in water saturation. The confusion arises because imbibition is used by other researchers to mean increase in the saturation of

a *wetting* phase, a distinction that is most meaningful in strongly-wetted systems. In mixed-wet systems, either water or oil may imbibe spontaneously, hence some arbitrary choices are necessary. Mixed-wet in this context means that not all surfaces in the rock have the same affinity for water and oil. Only in the special cases where water and oil both imbibe can mixed wetting be demonstrated, although it is probably true that mixtures of wetting conditions commonly exist in rocks filled with brine and crude oil.

There can be many reasons for contact angle hysteresis, including physical and chemical heterogeneity (Israelachvili, 1991). The crude oil components that can adsorb at oil/water and oil/solid interfaces will be reviewed in Chapter 2. Interactions between crude oil, brine, and rock (COBR interactions) that can contribute to hysteresis will be discussed in detail in Chapter 3.

If, on smooth surfaces, there is confusion because the contact angle is not unique, the situation in porous media is even more bewildering. Pore geometry is complex and pore walls are chemically heterogeneous. Heterogeneity on larger scales is a further complication that can have important implications for oil recovery. Recent studies by Huang *et al.* (1994; 1995) demonstrate the importance of wetting in laminated sandstones and even the existence of heterogeneous wetting. Wetting was inferred from matching detailed areal porosity, permeability, and saturation data to simulations. In the absence of such detailed information, wettability measurements are necessarily restricted to samples that are homogeneous on the core scale.

The lack of a direct measure of wetting in porous media exacerbates an already confusing situation. Two techniques have been most widely used to quantify COBR wetting: measurements of Amott indices (Amott, 1959), and the USBM method (Donaldson *et al.*, 1969). While variations of these two approaches have been in wide use, it has yet to be demonstrated that they are equivalent measures of wetting in porous media, or that indeed they should be.

Amott wettability indices

The wettability test proposed by Amott compares the amount of fluid that imbibes spontaneously with the amount of that same fluid that can be emplaced by centrifugation. Fig. 1-3 shows in general the relationship that might be observed between capillary pressure and water saturation.

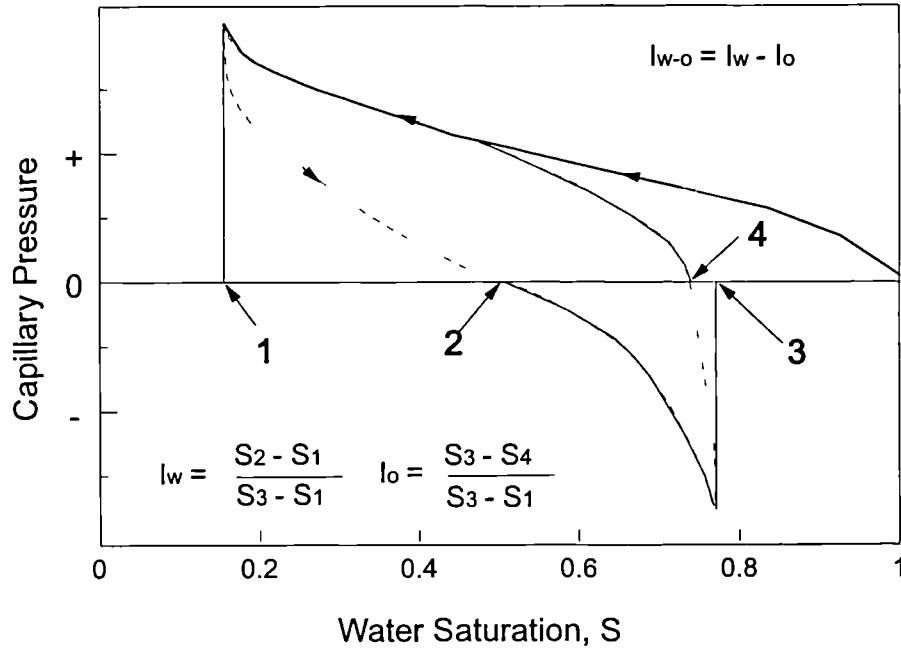


Figure 1-3. Schematic illustration of the changes in saturations with changes in capillary pressure that are measured to determine the Amott indices to water, I_w , and oil, I_o . The capillary pressures are not included in the indices and often are not measured.

If a core is completely filled with water, primary drainage begins at S_0 ($S_w = 1$). P_c increases as S_w decreases to some maximum value of P_c and minimum S_w , corresponding to the situation in an oil reservoir before production begins. This is the starting point for the Amott test. The curved line segment from S_1 to S_2 represents the change in capillary pressure that occurs with spontaneous imbibition of water, while the additional increase in water saturation from S_2 to S_3 occurs as water is forced into the pore space by gravitational forces in a centrifuge or by viscous forces in a coreflood apparatus. I_w is some fractional quantity between 0 (no spontaneous imbibition) and 1 (very strongly water-wet; no additional recovery by forced displacement). Similarly, spontaneous uptake of oil can be compared to the forced displacement of water by oil to give the Amott index to oil, I_o .

Many experimental details can have an impact on the values measured for Amott indices, including

- capillary pressure and saturations established during primary drainage,
- duration of spontaneous imbibition,
- adhesion of droplets of the expelled phase to the external surfaces of the core, and
- differences in techniques for forced displacements (e.g. viscous displacement, as suggested by Cuiec, 1975, instead of centrifuging).

Although any one of these factors may produce only a small shift in the Amott numbers, taken together they may account for significant biases. Results from one lab may show trends that are meaningful because all cores were treated identically, but comparisons between different laboratories might involve larger discrepancies due mainly to differences in experimental techniques or in core preparation and conditioning.

Bouvier and Maquignon (1994) found that I_w values measured in rocks from water, transition, and oil zones varied systematically with S_{wi} . For each set of cores, higher S_{wi} correlated with lower S_{or} as might be anticipated from well-known initial/residual relationships in water-wet samples. In addition, less water spontaneously imbibed as S_{wi} increased. Fig. 1-4 illustrates capillary pressure curves consistent with these observations and shows the cumulative effect toward lower I_w values. These effects would be superimposed on any real differences in wetting and might be more (or less) severe depending on the wetting conditions.

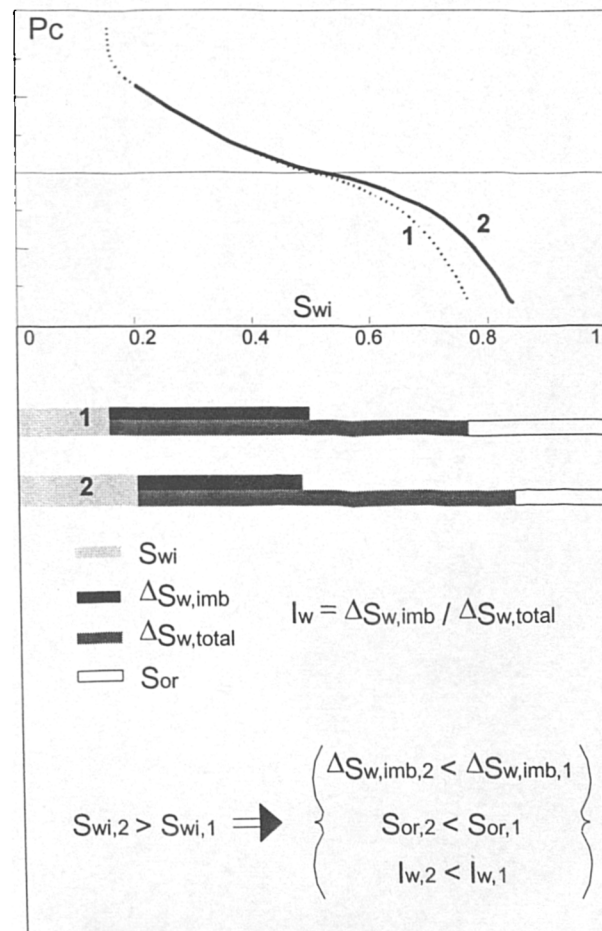


Figure 1-4. Starting Amott tests from different initial water saturations can lead to different I_w results.

There is little agreement with regard to the length of time required to complete the spontaneous imbibition steps in the Amott procedure and this too can shift the Amott index. Amott (1959) allowed imbibition for 20 hours. Anderson (1986b) recommends "that the cores be allowed to imbibe until either imbibition is complete or a time limit of 1 to 2 weeks is reached." This fails to resolve the question of how long is long enough. Zhou *et al.* (1993) showed wide variations of initial imbibition rate for Berea cores aged in crude oil. Allowed to imbibe for six months, however, all the cores in the study had reached the point where waterflooding produced no additional oil. In terms of the Amott test, therefore, all had $I_w = 1$ after six months of imbibition. Fig. 1-5 shows the rate of imbibition of water into a synthetic core treated with pH 4 brine and Alaska-93 crude oil (Buckley *et al.*, 1995). After almost two months, oil was still being evolved slowly. The Amott index to water measured at that time was $I_w = 0.5$, whereas a measurement after 20 hours would have been almost zero. Neither a standard, nor a "correct" length of time has ever been defined for these tests. Thus results can vary widely depending on the patience of the measurer.

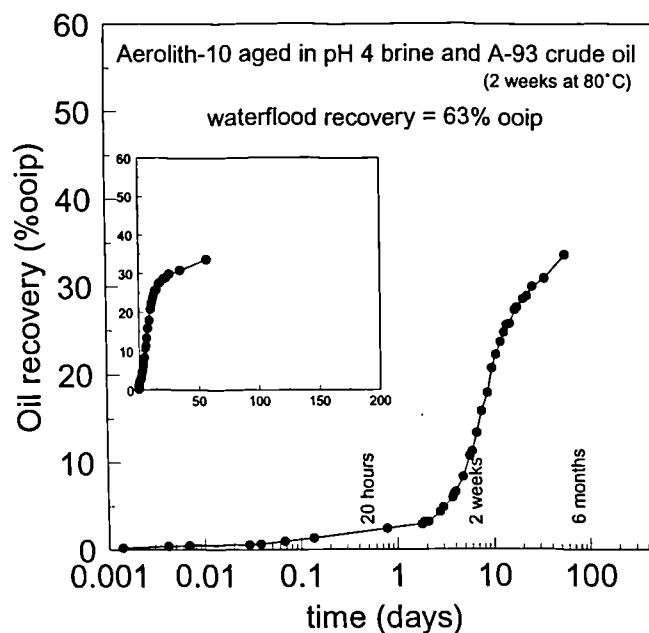


Figure 1-5. In cores that imbibe slowly, I_w will be affected by the imbibition time. Inset shows the same data on a linear time scale. Projection to 6 months imbibition time is shown by dotted extension. (data from Buckley *et al.*, 1995)

The two indices, I_w and I_o , can be combined to give the Amott-Harvey Index ($I_{w-o} = I_w - I_o$) which ranges from +1 for strongly water-wet to -1 for strongly oil-wet samples (Anderson, 1986b). Cuiec (1991) suggests broad classifications, based on the combined

index, as shown in Fig. 1-6. These same broad guidelines are sometimes assumed to apply to the USBM Index as well.

Amott Harvey Index					
$I_{w-o} = I_w - I_o$					
-1	-0.3	-0.1	+0.1	+0.3	+1
	slightly oil wet	neutral	slightly water wet		
oil wet	intermediate			water wet	

Figure 1-6. The Amott- Harvey Index defines broad ranges of wetting behavior. (after Cuiec, 1991)

USBM wettability index

Gatenby and Marsden (1957) observed that there should be a relationship between the areas under the capillary pressure curves and the work of displacing one fluid with another. The USBM wettability index was proposed by Donaldson *et al.* (1969) then working at the US Bureau of Mines. As shown in Fig. 1-7,

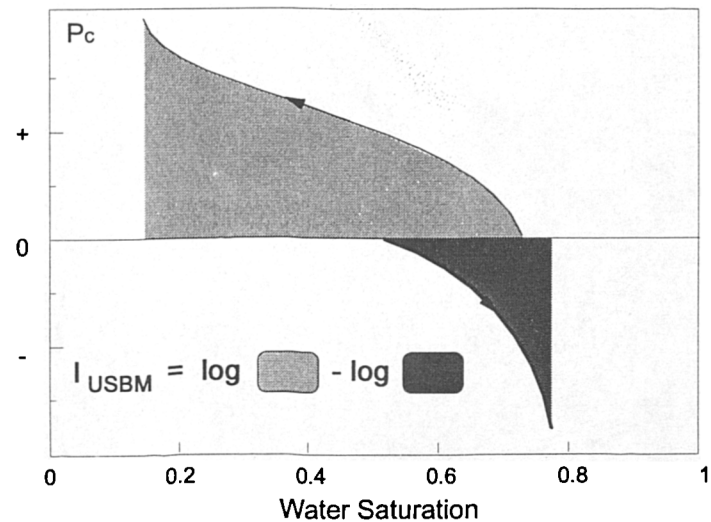


Figure 1-7. Illustration of the USBM Index measurement.

the secondary drainage (water saturation decreasing) and forced imbibition (water saturation increasing) data are measured by the centrifuge method and the logarithm of the ratio of the areas under these curves gives the USBM wettability index. Like the Amott-Harvey index, the USBM test results in a single number to describe wettability. The scale is positive for more water-wet samples and negative for more oil-wet ones. In principle, it can range from $-\infty$ to $+\infty$, but in practice values range from a low of about -1 to a high somewhat above +1. These analogies to the Amott-Harvey scale, coupled with the speed and convenience of the method, have led to its widespread use.

Practices have varied regarding whether average saturations or those calculated for the inlet face of the core (Hassler and Brunner, 1945) are used. Donaldson used the average saturations determined directly from the amount of water or oil expelled from the core, not

the equilibrium capillary pressure curves. Dullien and Fleury (1994) observe that the forced imbibition branch can never be considered an equilibrium capillary curve (even if the corrected saturations are used) since the pressure in the wetting phase is greater than that in the non-wetting phase. Although P_c vs S_w data are measured, the details of these curves are lost when the USBM index alone is reported.

Comparisons of the Amott and USBM indices

The USBM and Amott-Harvey indices were first compared by Donaldson *et al.* (1969). Measurements were made with crude oils with a wide range of viscosities (2.4 to 694 cp at 25°C). Separate core samples—both outcrop and reservoir sandstones—were used for Amott and USBM measurements. The results are shown in Fig. 1-8a. The three data points in quadrant III are the reservoir cores; all the others are outcrop samples. While there is general agreement on whether each sample is more water-wet (outcrop) or more oil-wet (reservoir), there is much less agreement on numerical values or even on the broad distinction between weakly and strongly wetted systems. Over half the measurements differ from one another by more than $\pm 20\%$. Hysteresis in the imbibition process, especially near neutral wetting, was suggested as the source of this lack of agreement. It was also suggested that the USBM—drainage-based—measurements should be considered the more quantitative.

Additional comparisons from subsequent use of these methods by other investigators have been collected in Figs. 1-8b through 1-8f. Sharma and Wunderlich (1985) measured Amott and USBM indices in a single experiment, so these comparisons are not only for the same core samples, but the same sequence of displacements (Fig. 1-8b). Average saturations were used for USBM index calculations. Agreement is good only for the most strongly water-wet samples. Several mixed-wet cores appear weakly water-wet in the USBM test, despite imbibing oil in the Amott portion of the test sequence.

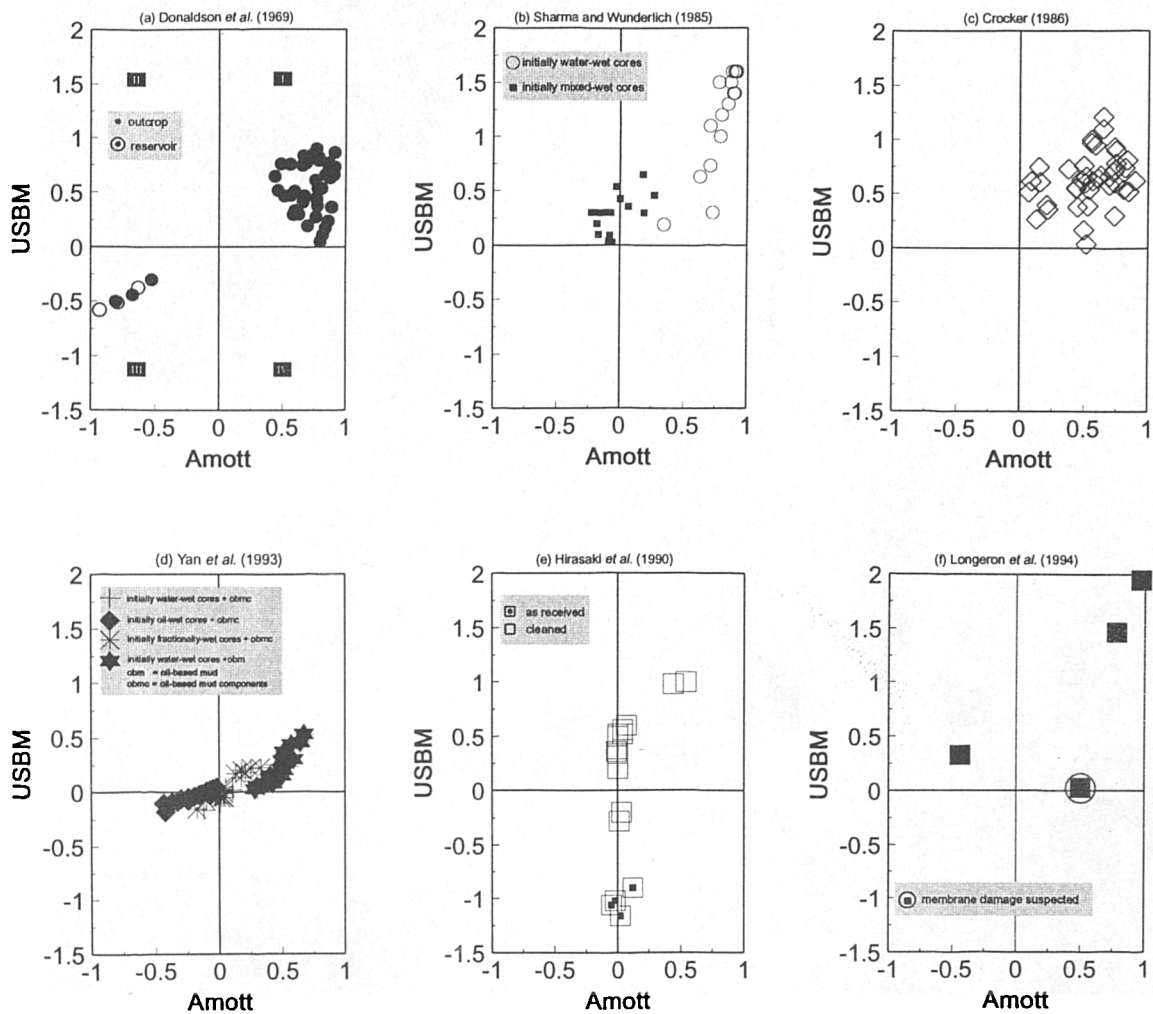


Figure 1-8. Comparisons of Amott-Harvey and USBM wettability indices.

Few experimental details were provided for the comparative measurements reported by Crocker (1986) that are reproduced in Fig. 1-8c. Crocker, like Donaldson, considered these results to be in good agreement, presumably because all fall in the preferentially water-wet quadrant in both cases. Regarding the extent to which samples might be strongly or weakly water-wet, however, there is little agreement between the Amott and USBM evaluations.

Yan *et al.* (1993) used the combined sequence of spontaneous imbibitions and centrifuge drainage displacements introduced by Sharma and Wunderlich. The USBM method was modified by the use of capillary pressure curves calculated for saturations at the inlet face of the core instead of the average saturation curves. Observations over the range

from weakly water-wet to weakly oil-wet are in much better agreement than any of the other published data (Fig 1-8d).

A combined Amott and modified USBM technique was also used by Hirasaki *et al.* (1990) with some further adaptations. The spontaneous imbibition steps were replaced by very slow spinning to overcome end effects caused by deposition of organic contaminants near the surfaces that occurred when solvent was dried from the cleaned cores. These results (Fig. 1-8e) suggest that significantly different properties are being measured by the two indices. The cluster of data points near the very oil-wet USBM value of -1 are initial measurements on the cores, as received. These cores imbibed both water and oil in small amounts, demonstrating their mixed-wet condition. After cleaning, most of the cores did not imbibe significant quantities of either fluid, though on the USBM scale, they range from weakly oil-wet to strongly water-wet.

In Fig. 1-8f, the USBM-type index is measured from drainage capillary pressure curves using a porous plate, rather than the centrifuge (Longeron *et al.*, 1994). The Amott indices were measured independently on different core plugs. As with other comparisons, agreement is best for strongly water-wet conditions and can lead to quite different conclusions about wetting otherwise.

Taken together, as in Fig. 1-9, the lack of agreement between these two measures of wettability is dramatic. Data for weakly water-wet samples fall almost anywhere in the first quadrant. Some cores that spontaneously imbibe more oil than water appear to be weakly water-wet in the USBM test. Whether this disagreement reflects the imprecision of these empirical tests or whether it may signify more fundamental differences between the properties being measured is a question that requires further consideration.

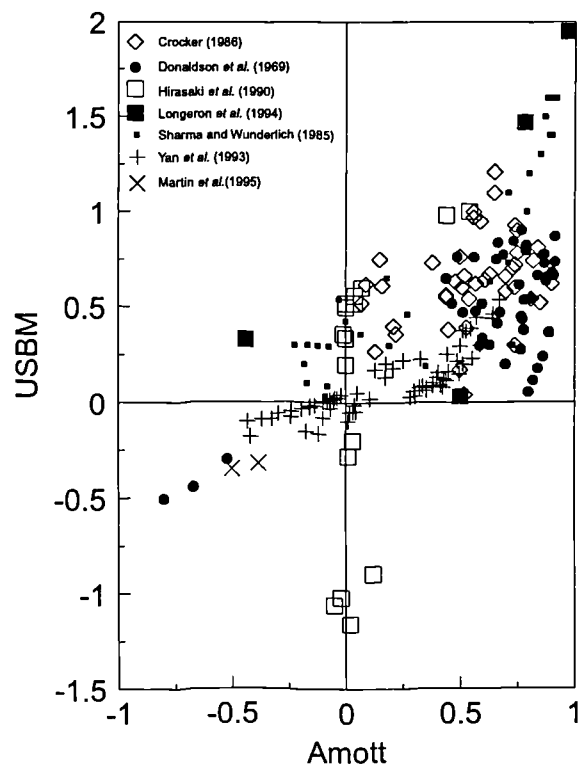


Figure 1-9. Collected comparisons of Amott-Harvey and USBM indices.

In some cases, discrepancies may occur because wetting can change over the time scale of the experiments. This is most likely if crude oils are used without a period of aging before the sequence of measurements begins. Sequential measurement of both Amott and USBM indices in a single series of experimental steps should minimize the differences that might occur from changes in wetting during the experiment. But even in the sequential comparisons, major differences in the indices are seen. It is important to recognize that different information is contained in these very different tests. Amott-Harvey and USBM indices cannot be used interchangeably as measures of wettability.

Improved methods of characterizing wettability

Only the extent of imbibition and the end points of the subsequent forced displacements are included in the Amott indices. The magnitude of imbibition capillary pressure and the rate at which a fluid imbibes can also be used as quantitative indicators of wetting within porous media. Morrow *et al.* (1994) have demonstrated a method using the rate of recovery by imbibition, with emphasis on the initial rate, as a measure of wetting. Spontaneous imbibition is clear evidence of preferential wetting in at least some connected pathways through the core. The method they outline is especially sensitive as wetting deviates from strongly-wetted conditions, a region in which the Amott test often fails to make clear distinctions. Their pseudo work of imbibition can be determined quickly and was shown to be a good predictor of improvements in oil recovery by waterflooding in the cases reported thus far, although the pore level mechanisms remain to be explained.

Areas under the imbibition capillary pressure curves are used in a new method demonstrated by Longeron *et al.* (1994). Using water-wet and oil-wet semipermeable membranes and controlled capillary pressures, the imbibition capillary pressure curve can be measured, but few data are as yet available.

Oil Reservoir Wettability

While the questions involved in determining reservoir wettability are not new, answers remain elusive. In part this is due to the absence of convincing *in situ* evidence regarding conditions in undisturbed reservoir rock. There is no clear standard by which to validate the results of laboratory experiments. Nor is there any simple model available that would permit systematic studies of the complex mixture of chemical constituents, fluid and solid, in oil reservoirs. Model systems fail to reproduce key features of crude oil/brine/rock ensembles. Empirical means of evaluating wetting in cores add confusion. Finally, it does

not help matters that the phenomena of interest often seem to be counter-intuitive. The presence of water, for example, can either prevent or enhance oil/solid interactions, as discussed in Chapter 3.

Are oil reservoirs strongly water-wet?

An intuitive approach once led to the supposition that all oil reservoirs are water-wet since water first occupied all of the pore space and oil entered as the non-wetting phase (Morrow, 1990). The convenience and reproducibility of doing laboratory experiments with refined oil under strongly water-wet conditions makes this an attractive scenario. Observations of other wetting conditions in laboratory tests with crude oils were ascribed to a variety of artifacts (temperature, pressure, and compositional changes during production, oxidation, or trace contaminants, to name a few). At least one case of strongly water-wet conditions has been documented: in the Athabasca tar sands, strong water-wetting has been preserved over geologic time (Takamura and Chow, 1983).

Standardizing on strongly water-wet conditions for laboratory testing has some advantages. Crude oils are complicated, changeable mixtures. Reconstructing a reservoir sample from produced fluids is an art in itself. Using mineral oil instead eliminates a major source of variability and permits reproducible studies of the influence of factors such as viscosity ratio, permeability variations, and flow rates. Scaling these results to conditions other than strongly water-wet, however, is not straightforward, thus limiting the usefulness of such studies.

COBR wetting

Low residual oil saturations in the East Texas reservoir stimulated work by Salathiel (1973) that led to the hypothesis that some oil reservoirs might be mixed-wet. Continuous pathways of both water-wet and oil-wet surfaces through the rock allow oil to drain down to very low oil saturations. This situation is quite different to either strongly water-wet conditions, where high saturations of oil can be trapped, or strongly oil-wet conditions, where early breakthrough of water can also result in high oil saturations remaining after waterflooding. In this view of mixed wetting, pore size and fluid distributions are crucial in determining the pattern of wetting that evolves. The smallest pores remain water-filled and water-wet. Larger pores fill with oil and, over geologic time, can become oil-wet.

Continuous networks of both water-wet and oil-wet pathways can be explained, assuming that wetting is altered by adsorbing molecules that are not able to affect the surface except in the areas of direct contact. Whether or not there is direct contact depends on

whether water films are stable which in turn depends on the balance of van der Waals, electrostatic, and other forces (Buckley *et al.*, 1989) and on capillary pressure (Hirasaki, 1991). This is the picture of wettability alteration assumed by Kovscek *et al.* (1993) which leads to capillary pressure vs. saturation relationships that resemble those for mixed-wet rocks.

The effect of mineralogy may lead to another distribution of wetting. Some mineral surfaces may be more reactive with crude oil components than others. Depending on the distribution of these reactive minerals, a fractional wetting can be envisioned where there need not be connectivity of oil-wet surfaces. Combinations of these and other mechanisms of wetting alterations lead to a complex taxonomy of wetting conditions that have as yet been only partly differentiated and described.

Early work on wetting of oil reservoir rocks and fluids was reviewed by Taber (1980) who pointed out both the importance of capillary forces and the confusion over the effects of wettability. In 1986 and 1987, Anderson provided an extensive review of the wettability literature (Anderson, 1986a,b,c, 1987a,b,c) which illustrated the same points, but left many important questions unresolved about the wetting states that can occur in crude oil/brine/rock ensembles and their effect on oil recovery. More recent reviews by Morrow (1990) and Cuiec (1991) provide both historical perspective and critical assessment of the current state of wettability research. Significant advances have been made, especially in appreciation of the implications of mixed-wet conditions. These extensive reviews are in agreement that, despite the large volume of work on COBR wetting phenomena, significant gaps remain in our understanding of both its causes and effects.

Reservoir wetting

It may be that, because of the complexity of reservoir wetting, the best way to establish conditions in a particular reservoir is to examine samples of rock and fluids under reservoir conditions of pressure, temperature and confining stresses. Exact duplication is, of course, never achieved. Technical and economic factors both influence the extent to which reservoir conditions testing approaches reservoir conditions. These tests, however exacting, can never answer the one key question: how close is close enough?

Two approaches are commonly used in reservoir conditions tests: (1) preservation of wetting and fluid saturations during recovery and handling of the core, and (2) restoration of wetting and fluid saturations in cleaned reservoir cores. Preservation requires much more careful and prompt core handling than is normally available. Only the portion of core that

is uninvaded by drilling fluid really preserves reservoir conditions and then only if temperature and pressure are maintained. Given the stringent requirements for preservation, restoration may seem a more feasible alternative, but it has limitations as well. Restoration requires that the core can be cleaned, that the correct water saturation can be reestablished, that the COBR interactions that established wetting in the reservoir occur with the components in the produced oil, and that they occur over relatively short periods of time. Neither preservation nor restoration can guarantee duplication of reservoir conditions. Cuiec (1991) recommends doing both and comparing the results, but time and expense may limit adherence to these guidelines, and there still remains the possibility that the results are not representative of the reservoir.

A somewhat different approach is explored in this thesis. Here we focus on the mechanisms that control COBR wetting. With improved understanding of those mechanisms we may be better equipped to design laboratory experiments that provide relevant displacement properties for real reservoirs without the necessity of recreating that reservoir in the laboratory.

Modes of Wetting Alteration

Benner and Bartell (1941) recognized that polar components in crude oils can be acidic or basic in character and that either can interact with rock mineral surfaces to alter wetting. Bartell and Niederhauser (1949) isolated some of the surface active material from crude oil and concluded that it resembled material in the asphaltene and resin fractions. Work since that time has shown general agreement that polar oil components *can* affect wetting, but less agreement has been reached regarding when they *do* alter wetting.

The number of combinations of oil components, brine ionic species, and surface minerals is very large. Perhaps this has contributed to the confusion that is reflected in the large body of often conflicting literature (Anderson, 1986a-c, 1987a-c). Progress is being made, however, in identifying the full suite of variables that must be considered in concert, rather than separately, to produce the wetting effects observed with natural materials. Gradually the reasons for the confusion and the underlying similarities between different crude oils are emerging.

The pore space in most reservoir rock was initially filled with brine. Oil displaces water during filling of the reservoir. In principle, oil components could then interact with the rock surfaces in several ways: adsorption from the oil phase, adsorption through the water

phase, deposition of an insoluble monolayer formed at the oil/brine interface, or precipitation of oil-wet solids. Each of these possible modes of interaction, illustrated in Fig. 1-10, has somewhat different implications for the strength and reversibility of adsorption and the types of crude oil components most likely to be involved. Indeed, additional multi-step mechanisms of wetting changes involving different rates for smaller and larger molecular weight polar species can also be envisioned.

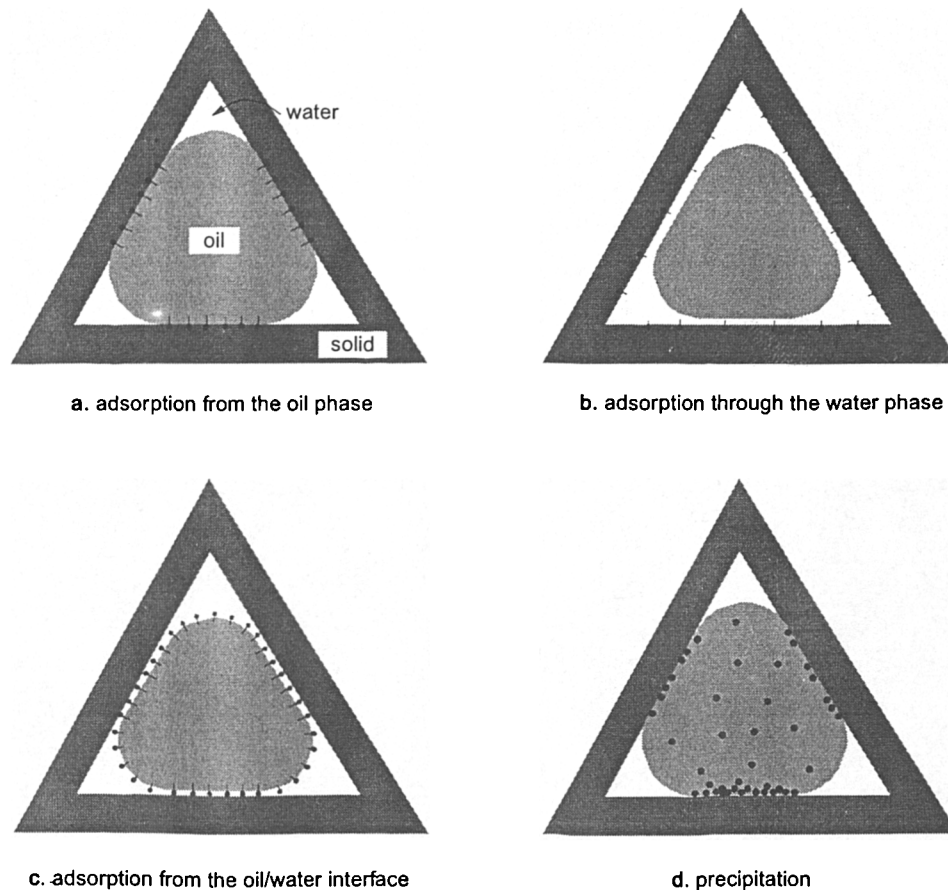


Figure 1-10. Possible mechanisms of COBR wetting alteration.

a. Adsorption from the oil phase: If oil contacts rock surfaces, adsorption from the oleic phase can occur. Surface active material can adsorb on solids from nonaqueous solution to form monolayers, swollen monolayers, or even multiple layers, in complex interactions that can be highly influenced by even small amounts of dissolved water (Chen, *et al.* 1992b). The approach to equilibrium can be slow as shown by surface forces measurements between mica surfaces in crude oils (Christenson and Israelachvili, 1987).

The first question that arises is how, in an initially water-wet rock, does contact between oil and solid occur? In special cases, rock surfaces may be oil-wet initially, either (1) because of specific oil-wet minerals (Anderson, 1986a, lists minerals that are hydrophobic

at air/water interfaces) or (2) because the rock is both source and reservoir (Cuiec, 1986) and thus has organic coatings on pore surfaces. It is unlikely, however, that wetting conditions of most reservoir rocks can be explained by either of these special cases.

DLVO forces, the combined effect of van der Waals and electrostatic interactions, have been shown to affect the stability of a layer of water between solid and oil (Buckley *et al.*, 1989). Predictions of water film stability are most accurate when salinity is low, limiting application of DLVO theory in many practical situations. The questions of access of the surface to oil components and the role of water in mediating oil/solid interactions are the focus of Chapter 3.

If direct contact does occur, there is experimental evidence showing that asphaltenes adsorb on mineral surfaces, especially clays. Some important variables that affect adsorption include the type of clay and its exchangeable cations, nitrogen content of the oil, and the solvent in which the polar compounds are dissolved (Clementz, 1976, 1982; Czarnecka and Gillott, 1980). The presence of water does not prevent interaction, but bulk water can reduce the extent of adsorption (Collins and Melrose, 1983). Monolayer adsorption was observed, except in nitrobenzene, which is a polar solvent. The thickness of the monolayer depends on the solvent from which it was adsorbed (Dubey and Waxman, 1989). Studies designed to separate out the effects of acidic and basic components (Denekas *et al.*, 1959) or various distillation fractions (Cuiec, 1986) in different lithologies have demonstrated the complexity of the interactions involved in these adsorption processes.

It is important to consider to what extent studies such as these, from which water was mostly excluded, are representative of processes that occur in an oil reservoir where water is always present. In Chapter 2, examples of adsorption of crude oil components onto dry surfaces will be presented. These results will be compared to studies of the same crude oils and solids in the presence of water in Chapter 3. Contact angles measured after adsorption suggest that the processes occurring under dry conditions are different in nature and extent to adsorption in the presence of water.

b. Adsorption through the water phase: Oil components may be extracted from the oil into the water phase, or otherwise "cross through the water film," eventually to be adsorbed onto rock surfaces (Cuiec, 1986). Anderson (1986a) suggests this mechanism, citing evidence in the literature that shows everything from enhanced to eliminated interactions when water is present, without explaining the diversity of results.

Whether extractable components can adsorb to produce oil-wet conditions on initially water-wet surfaces will be considered further in Chapter 3. Since the most water-soluble components have likely been removed by extraction before the oil is produced, negative evidence of studies with laboratory samples cannot be considered conclusive. Nonetheless, it is worthwhile to note that we have as yet to encounter an oil sample whose water-extract can produce oil-wet contact angles.

Rueslåtten, *et al.* (1994) suggest a somewhat different mechanism for wetting alteration through a bulk water phase that involves precipitation of organo-metallic complexes during oil migration into the reservoir. Reservoir cores, which could not be cleaned to more water-wet conditions with organic solvents, were shown to be cleaned by treatment with complexing agents.

If adsorption can occur through the bulk water phase, the consequent pattern of wetting might be uniform (all surfaces altered to approximately the same extent), if the oil components control the process, or fractionally-wetted, if surface mineralogy is the controlling factor. Both of these conditions are different than the Salathiel-type of mixed-wetting with continuity of both oil-wet and water-wet pathways. Distinguishing between these different wetting conditions is not an exact science, but imbibition of both oil and water, reported for freshly-recovered reservoir cores (Wunderlich, 1991) would seem to require mixed-wetting of the latter type.

c. Adsorption from the oil/water interface: Acidic and/or basic substituents of large organic molecules can exist as ions at the oil/water interface. Thus assembled, they may be deposited onto the solid surface by a mechanism analogous to Langmuir-Blodgett deposition of a surfactant film on a solid as it passes through an air/water interface (Chen *et al.*, 1992a). Strong ionic interactions—either attractive, repulsive, or both—would result. In some cases interfacially adsorbed species are seen as rigid films (Reisberg and Doscher, 1956). More detailed consideration of species present at the oil/water interface will be presented in Chapter 3.

d. Precipitation: Although wetting alteration is often suggested as a consequence of precipitation of asphaltenes, precipitation, per se, has not been demonstrated to contribute to reservoir wettability on a broad scale (Buckley, 1993a). Even cases of extensive organic deposition, such as may occur with some crude oils during enhanced recovery with carbon dioxide, have not been firmly linked to wetting alteration (Wolcott, 1993). Wetting alteration

can be demonstrated under conditions where asphaltene stability is assured so precipitation, while it may be a contributing factor, is not a requirement for COBR wetting effects.

Depending on extent, precipitation might plug pore throats and alter reservoir rock beyond its effect on wettability. Separating the coupled effects of wetting and permeability alteration is non-trivial, and accounts in the literature are not always clear in this regard. It is also unclear what the pattern of altered wetting would be. Micromodel studies have shown, in one specific instance, that solids can remain suspended in the oil phase and are transported or trapped with the oil (Buckley, 1993a). The state of the asphaltic material in a crude oil may well influence COBR wetting alteration (as shown in Chapter 2), but it need not be assumed that precipitation is the mechanism by which the oil/solid interaction occurs.

Interpretation of Wetting Alteration Effects

Wettability is seldom a concern in and of itself; it is the effect that wetting has on movement of oil by water or other fluids and ultimately on oil recovery that is of practical interest. Prediction of oil recovery relies on simulations in which wettability information is usually encoded in the form of relative permeabilities and capillary pressures. While these functions, k_{rw} , k_{ro} , and P_c , are certainly related to wettability and to oil recovery, the relationships are not as simple as sometimes assumed. The rules of thumb outlined by Craig (1971) are summarized in Table 1-1.

Table 1-1. Rules of thumb for water and oil-wet formations. (from Craig, 1971)		
	Water-Wet	Oil-Wet
S_{wi}	> 20 - 25%	< 10 - 15%
$S_w (k_{rw} = k_{ro})$	> 50%	< 50%
$k_{rw} (S_w = 1 - S_{or})$	< 30%	> 50%

These simple rules, which divide reservoirs into water-wet, oil-wet, and intermediate (no strong preference for either water or oil), do give some idea of the shifts of residual saturations and relative permeabilities with wettability, but are insufficient to explain the wide variety of wettability effects on oil recovery summarized by Morrow *et al.* (1986) shown in Fig. 1-11. The data assembled by Morrow *et al.* (1986) that are reproduced in Fig 1-11 represent comparisons of oil recovery efficiency (i.e., the fraction of oil originally in

place that is recovered) for cores where non-water-wet and strongly water-wet comparisons were available. While there is not conclusive evidence of the wettability states in all of these cases, it does appear that those for which recovery was improved over strongly water-wet conditions are the weakly water-wet (possibly mixed-wet) cases, whereas recovery from more oil-wet cores was generally poorer than from comparable, strongly water-wet cores. It is clear that alteration of wetting can have a significant impact on oil recovery, but, as this comparison emphasizes, it has been much less clear how wettability and oil recovery are related.

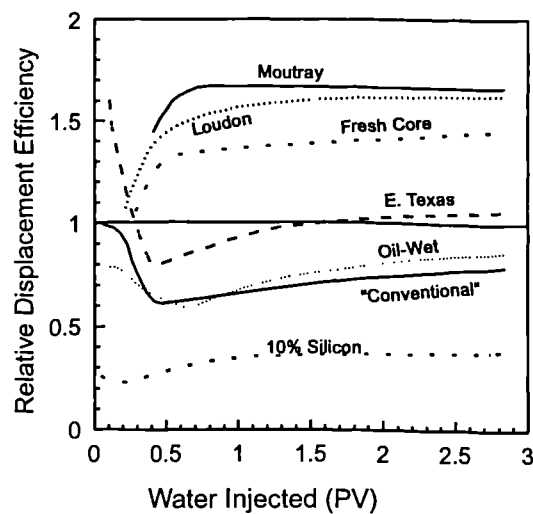


Figure 1-11. Displacement efficiencies of nonwater-wet waterfloods compared to a waterflood under strongly water-wet conditions. Oil recovery can be considerably greater or less than in comparable strongly water-wet floods. (after Morrow *et al*, 1986)

Using spontaneous imbibition to characterize wetting of COBR ensembles, Jadhunandan and Morrow (1995) demonstrated that oil recovery efficiency in Berea sandstone is at a maximum when I_{w-o} is slightly greater than zero (Fig. 1-12). Results that appear to contradict the trend established for Berea are illustrated in Fig. 1-13 for waterfloods under more and less water-wet conditions in a synthetic porous medium. Investigations of these complex relationships between wetting, pore geometry, and oil recovery, and interpretation based on network models (Dixit *et al.*, 1996) are presented in Chapter 4.

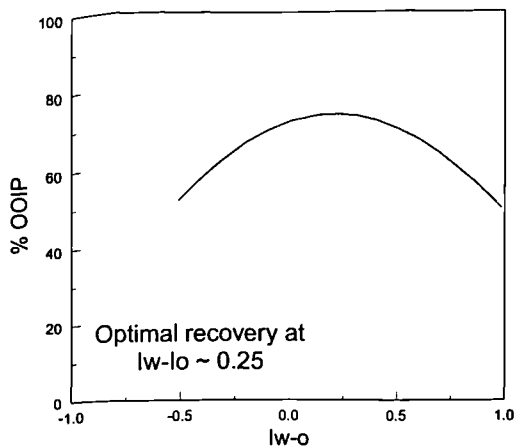


Figure 1-12. Oil recovery efficiency first increases, then decreases as Berea sandstone cores become less water-wet. Data shown are for recoveries after 3 PV of water. (after Jadhunandan and Morrow, 1995)

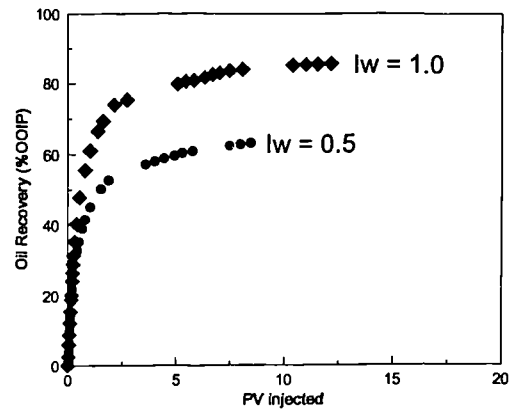


Figure 1-13. In a synthetic core, waterflood displacement efficiency is higher for the more water-wet core.

Pursuit of simple relationships between wettability and oil recovery have historically been plagued by two kinds of logical errors. First is the mistake of interpolating between results from the extremes of strongly water- and oil-wetted systems to predict flow parameters for mixed-wet conditions. As Fig 1-12 makes clear, oil recovery at weakly water-wet conditions is not half-way between strongly water-wet and strongly oil-wet. The second common problem occurs when we try to deduce wetting conditions from changes in relative permeabilities or residual saturations that could as well be explained by other, perhaps unintended, changes in the system. An example may help to illustrate the confusion that arises.

The capillary pressure curves shown in Fig. 1-14 (Olsen *et al.*, 1991) were obtained by centrifuging air into brine-filled Berea sandstone cores at temperatures from 75 to 350°F. Over that range, there is a shift in S_{wi} , the minimum water saturation after centrifugation from 20 to 35%. This shift is interpreted—consistent with the rule of thumb—as an increase in water-wetting with increasing temperature. Since the air/brine/Berea sandstone system is very strongly water-wet at 75°F, it is unlikely that the shift in S_{wi} is caused by a change in wetting. The rules of thumb can tell us how S_{wi} (or relative permeability functions) may be expected, in general, to change with wetting, but the reverse process, using them to attribute to wettability an unexpected change in S_{wi} , can lead to considerable confusion.

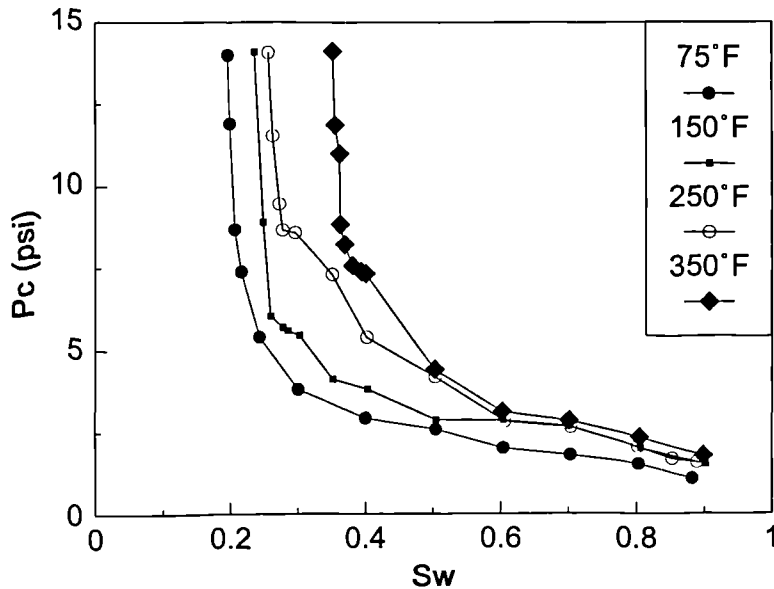


Figure 1-14. Changes in centrifuge capillary pressure curves with temperature for Berea sandstone measured with brine and air. (after Olsen *et al.*, 1992)

Summary and Organization of the Thesis

In summary, wettability is a very important factor affecting oil recovery. However, interpretations have been fraught with difficulty because of the complexity of interactions in the COBR systems and in the variable consequences of these interactions in terms of the macroscopically observable oil recovery that results. The study of wettability and its effect on oil recovery has therefore suffered from the following problems:

- i. many confusing and apparently contradictory observations,
- ii. the lack of a clear standard test for wettability which is clearly understood theoretically,
- iii. a good understanding of the fundamental mechanisms of wetting and wetting alteration in COBR systems,
- iv. a knowledge of how different pore scale mechanisms of wettability lead to a taxonomy of wetting conditions and how macroscopic consequences follow in a predictable way.

The study in the remainder of this thesis is focused in parts (iii) and to some extent (iv) above. Interactions between fluids and smooth surfaces, glass micromodels, and core test results are presented in order to clarify the underlying mechanisms which operate in COBR systems. The consequences of such changes to macroscopically observable results must be translated through some level of modelling, either at the pore or macroscopic scale.

However, care must be taken in ascribing changes in large scale parameters (relative permeability or capillary pressure functions) to wettability since other factors may also influence these relationships.

In order to understand how variables such as aging temperature, aging time, or brine composition can affect COBR wetting, a two-stage approach is needed. First, studies of the interactions, as they affect the wetting of flat surfaces, are needed. These studies segregate the interactions without the added complications of pore geometry and interconnectivity. Then we need to be able to show how the flat surface interactions get translated into COBR wetting. This two-stage approach, relating flat surface observations to wetting alteration in porous media, is the foundation of this thesis.

The thesis progresses from the simpler to the more complex. Chapter 2 is focused on the polar constituents of crude oils that are available to influence wetting, and on the crude oil environment that influences the behavior of those polar components. In Chapter 3, the roles of water are examined, first at the oil/water interface, then in the presence of a solid surface. The added complexities of the porous media will be examined first in relatively simple micromodels and finally in synthetic cores and in sandstones (Chapter 4). The aim is to tie observations of COBR wetting in rocks back to the flat surface wetting measurements. Finally, in Chapter 5 some mechanisms of COBR wetting interactions are proposed.

Although interrelated, each chapter is an independent unit with introductory material, experimental results, and conclusions. Details of more general applicability (fluid properties, some experimental methods, etc.) are segregated into appendices to facilitate reference. Many aspects of brine geochemistry, rock mineralogy, and heterogeneity are beyond the scope of this thesis, although their impact upon COBR interactions is recognized. In fact, the central finding of this work is that the compositions of all three phases—oil, brine, and solid—are important and meaningful studies must consider all three of these together.

Chapter 2

THE COMPONENTS OF CRUDE OILS THAT INFLUENCE WETTABILITY

Crude oils contain chemical species that can adsorb on high-energy mineral surfaces. The nature of those components, their occurrence in crude oils, and mechanisms by which they may interact with solids are the focus of this chapter. Interactions depend, not only on the chemical identity of the polar species, but also on the solvent quality of the oil as a whole. The solvent environment can influence wetting alteration by changing the state of dispersion of the polar crude oil constituents. An experimental method for quantifying the solvent properties of crude oils concludes this chapter.

Crude Oil Composition

Crude oils are complex mixtures of hundreds of components ranging in size from one carbon atom to one hundred or even more. Beyond the first few members of each homologous series, individual species cannot be readily separated and identified by standard techniques. Instead, crude oils are often characterized by dividing components into a few groups based on physical and chemical separations.

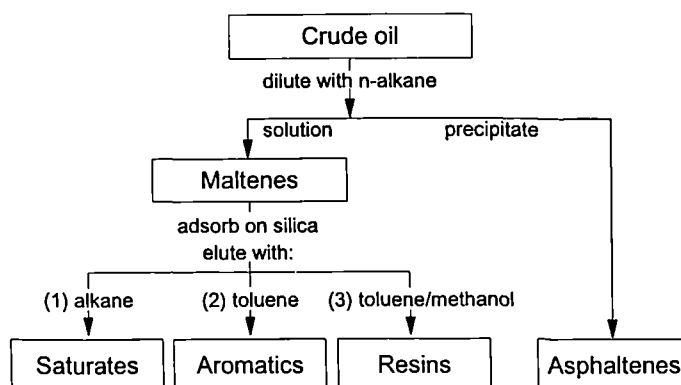


Figure 2-1. SARA separation scheme divides crude oil into Saturates, Aromatics, Resins, and Asphaltenes.

One of many such separation schemes is shown in Fig. 2-1 (adapted from ASTM D2007-80). Some of the heaviest, most polar components are insoluble in low molecular weight paraffins. If one volume of crude oil is mixed with 40 volumes of n-pentane, the resulting precipitate is defined as the asphaltene fraction of the oil. The remainder of the oil can be separated chromatographically on the basis of polarity, with saturates as the least

polar fraction, followed by the aromatic hydrocarbons. The final fraction, called resins or polars, consists of hydrocarbons with small percentages of polar heteroatoms (mainly oxygen, nitrogen, and sulfur).

An oil composed only of saturates and aromatics would be nonwetting relative to water on most clean mineral surfaces. The best evidence for strong water-wetting of outcrop sandstones is the rate at which water imbibes into an oil-filled rock. For a refined oil in Berea sandstone, this can be very rapid indeed. Hence, attention with respect to wetting, has focused on the asphaltene and resin fractions, both of which have polar components that can adsorb on silica and other mineral surfaces.

Some mechanisms by which these polar compounds may interact with solid surfaces in pores that are initially filled with water or brine were discussed in Chapter 1. Wetting alteration on initially dry surfaces has been reported; the fairly unspecific nature of these interactions will be demonstrated. The chemical nature of the asphaltene and resin fractions, especially their polar functionality, will be reviewed in this chapter. The acid/base interactions of these polar components, that become important only when water is also present, will be discussed further in Chapter 3.

Interactions among the compounds in the asphaltene and resin fractions and of those same compounds with solids, are very sensitive to the solvent environment within the crude oil itself. The solvent properties of the oil are shown to be quantifiable by reference to the mixture refractive index. The onset of asphaltene precipitation from mixtures of crude oil and solvents is shown to occur at a constant value of refractive index that depends on the precipitant. The main purpose of Chapter 2 is to set the stage, with respect to the unique attributes of crude oils, for consideration of the complex interactions in crude oil/brine/rock ensembles that follow in Chapters 3 and 4.

Asphaltenes and Resins—Polar Components that Can Alter Wetting

Resins and asphaltenes represent a continuum of crude oil species that are high in molecular weight and somewhat polar. Chemical compositions of either asphaltenes or resins depend on the source crude oil as well as the method by which the fractions were separated from the remainder of the oil. The distinction between them is based on solubility. The molecules that precipitate in response to addition of different diluting agents represent a balance of polarity, aromaticity, and molecular weight (Long, 1981; Cimino *et al.*, 1996),

as shown schematically by the various shaded areas in Fig. 2-2. Reported molecular weights are usually for aggregates, rather than single molecules, and vary from a low of around 1000 to highs in the hundreds of thousands of Daltons (Speight *et al.*, 1985).

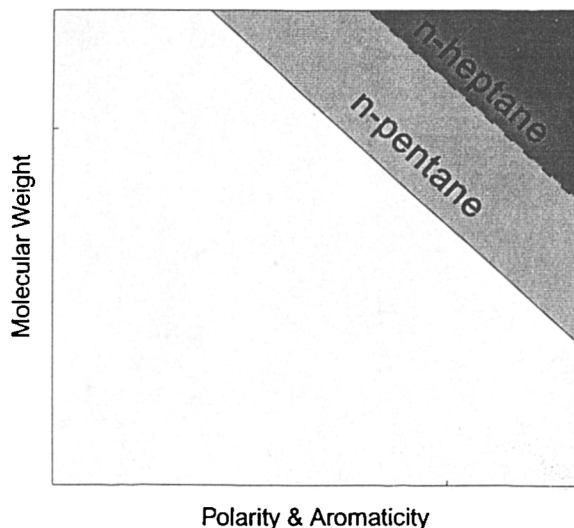


Figure 2-2. General characteristics of asphaltene precipitates. Above and to the right of each line is the material that precipitates. (after Long, 1981, and Cimino *et al.*, 1996)

While the absolute molecular weight of molecules in the asphaltene fraction is difficult to measure, the ratio of elements is fairly consistent for asphaltenes from a wide range of sources (Speight, 1980), and on average can be represented by an empirical formula which, for the n-pentane precipitate, is $C_{100}H_{115}N_1S_3O_2$. The hydrogen to carbon ratio indicates a high degree of aromaticity, nitrogen content varies only a little, while oxygen and sulfur are more variable. None of these polar constituents is present in sufficient quantity to confer significant water solubility on such large organic molecules, but the extent of polar functionality may well contribute to the affinity of these molecules for the oil/brine interface (Chapter 3).

Most of the detailed chemical information available concerns the asphaltenes (e.g., Speight and Plancher, 1991), rather than the resins. Oxygen occurs in carboxylic acids, as phenols, and as keto groups. Nitrogen is found in heterocycles of various types, including pyridine derivatives with basic character and non-basic pyrrol-type rings. Sulfur is found in heterocyclic thiophene condensed ring systems, and as sulfides, linking both alkyl and aryl moieties. Functional groups that contain both nitrogen and oxygen, including cyclic amides (for example, 2-quinolone), may provide amphoteric (groups that can act as either acids or

bases) or even zwitterionic (simultaneously positively and negatively charged) sites. Physisorption may occur through weak dipolar interactions with any of these kinds of heteroatomic functional groups. Stronger ionic interactions are restricted to those that can be positively or negatively charged.

Adsorption onto Dry Surfaces

Adsorption of crude oil components can alter the wetting of dry solid surfaces. The extent of wetting alteration, as judged by contact angles between water and decane, are shown in Fig. 2-3 for several different crude oils (Liu and Buckley, 1995; Liu, 1993). The physical properties of these and other crude oils are summarized in Appendix A. Glass slides were cleaned, dried, and aged in crude oils for varying lengths of time, at either room or elevated temperature. After the aging period, bulk crude oil was removed from the surface by rinsing with toluene. The rinsed slide was immediately submerged in decane and the contact angles were measured with a captive drop of distilled water. Details of the adsorption experiment can be found in Appendix B.

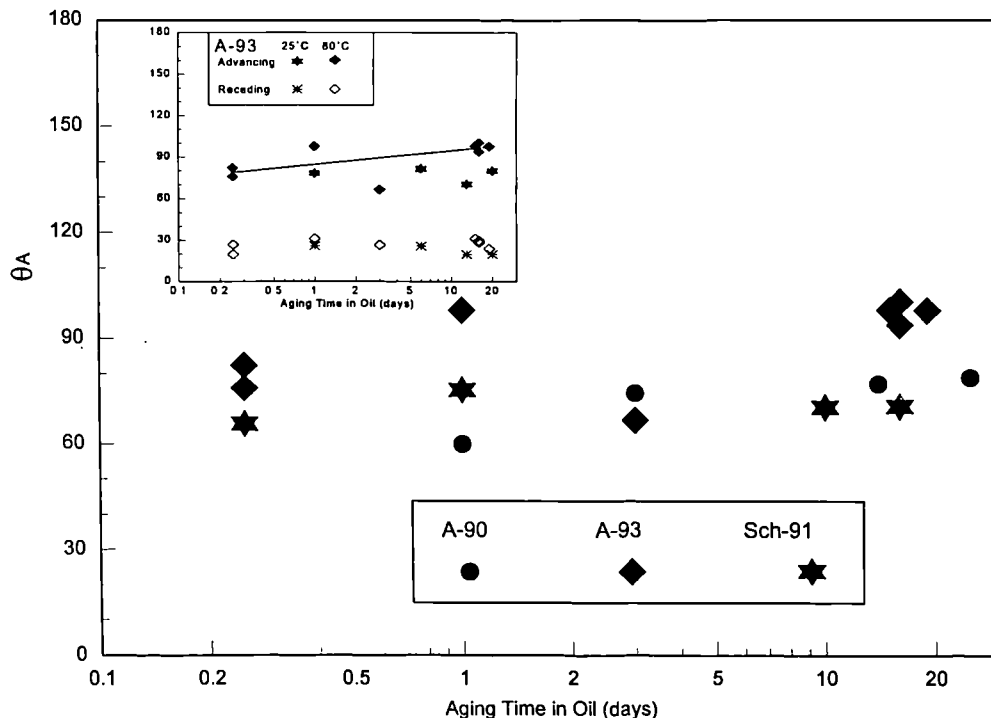


Figure 2-3. Adsorption from crude oil onto dry glass surfaces at 80°C for three different crude oils. Inset shows the effect of temperature on adsorption of A-93 crude oil and the hysteresis between advancing and receding contact angles.

As shown in Fig. 2-3, water advancing contact angles on surfaces that were aged in three different crude oils at elevated temperature (80°C) are spread over a small range from a low of about 60 degrees to a high of less than 100 degrees. All of these values fall within the intermediate wetting range. Aging times ranged from as short as 6 hours to as long as 3 weeks.

It will be of interest to note, when these results are compared in Chapter 3, to adsorption onto surfaces that are initially exposed to various brines, that for the dry surfaces, there is little effect of either aging time or of aging temperature (see inset to Fig. 2-3). There is substantial hysteresis between advancing and receding conditions. Overall, adsorption of crude oil components onto dry glass surfaces is quick, does not change much with either aging time or aging temperature, but does vary (over a small range of intermediate angles) for different crude oils.

Colloidal Dispersion of Asphaltenes

Both asphaltenes and resins exist in crude oil as aggregates. The colloidal nature of asphaltenes was postulated in early studies by Nellensteyn (1938) and by Pfeiffer and Saal (1940). More recently, measurements with small angle x-ray (SAXS) and neutron (SANS) scattering (Espinat and Ravey, 1993; Thiyagarajan, 1995) have demonstrated the changes in aggregation size with changes in temperature or solvent. Fig. 2-4 shows nominal volumes measured by these techniques for asphaltenes from two different oils (Safanya and Maya) dissolved in various solvents. The volumes were calculated directly from the published size parameters to allow a rough comparison between results from different groups of investigators who have interpreted their data using different shapes as models (including disks, rods, and spheres). As shown in Fig. 2-4a, asphaltene aggregates dissolved in toluene were observed to increase in size with increasing fractions of a precipitant (n-heptane) added to the mixture. Fig. 2-4b shows the opposite effect of adding resins which are good asphaltene solvents. Increasing temperature (Figs. 2-4 c and d) also decreased the size of aggregates.

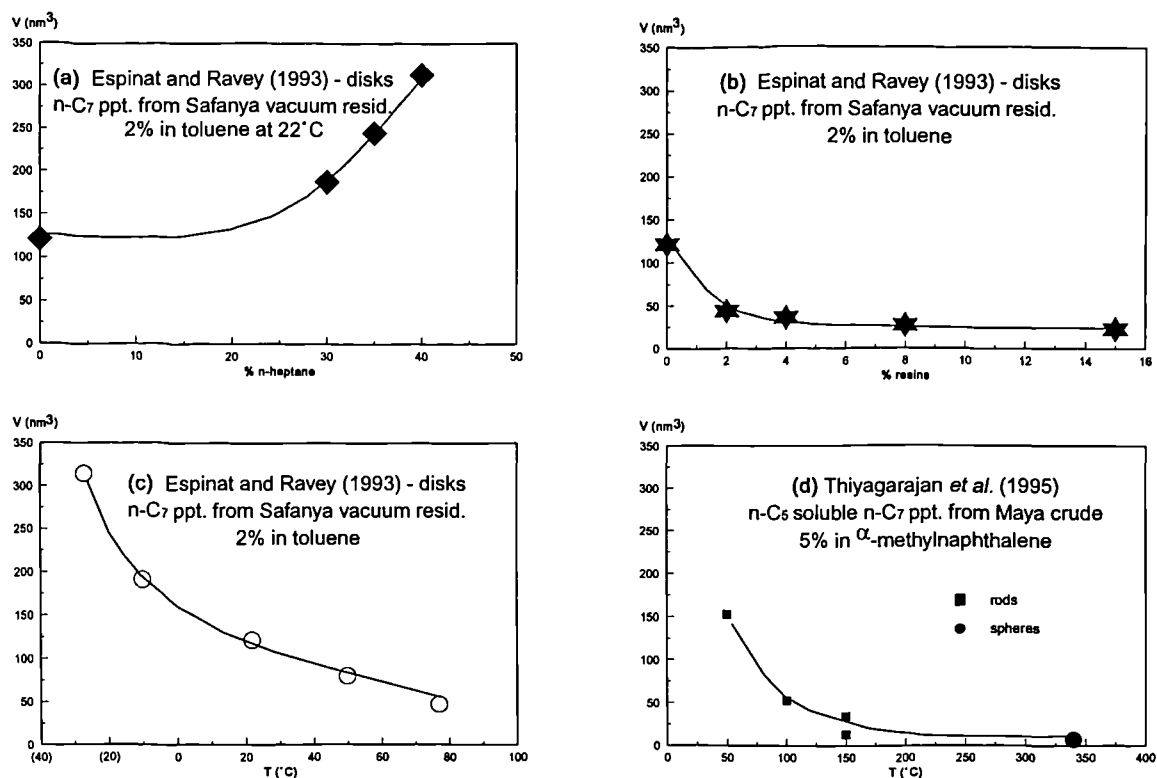


Figure 2-4. Variation in size of asphaltene aggregates with changes in solvent properties and temperature (determined by small angle neutron scattering, SANS, experiments). Nominal volumes were calculated on the basis of reported dimensions and shapes.

It has long been speculated that resins are required to keep asphaltenes in suspension, i.e., that resins peptize the asphaltenes. Resins coprecipitate with the asphaltenes when the oil is diluted with a precipitant such as n-pentane, but redissolve upon washing with additional precipitant (Speight and Moschopedis, 1981). Comparisons of the amounts of each of these two fractions in some crude oils, as reported in several different sources in the literature, are shown in Fig. 2-5. While there is not a simple relationship between the two fractions, it does appear that crude oils with the least resins have little or no asphaltenes. There is, however, no direct evidence to support the common supposition that stripping of resins from the asphaltene aggregate, illustrated in Fig. 2-6, is the mechanism by which destabilization of the asphaltenes occurs.

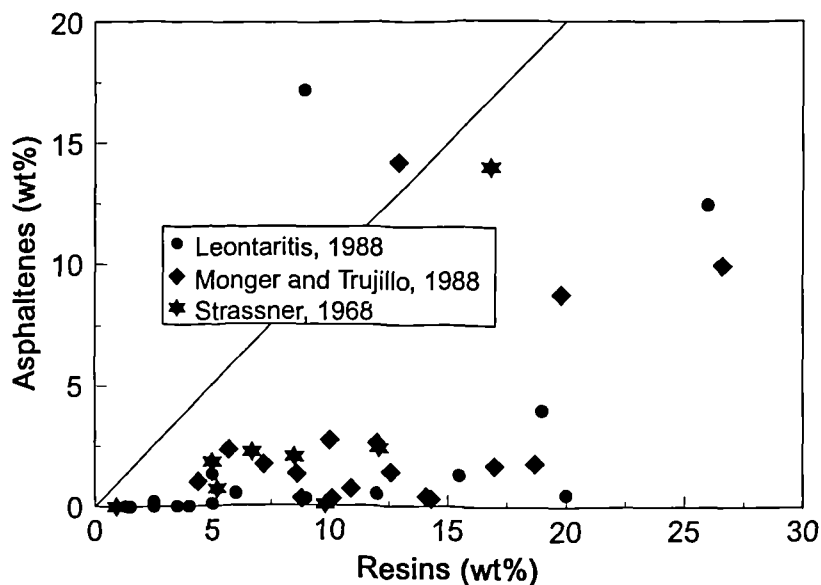
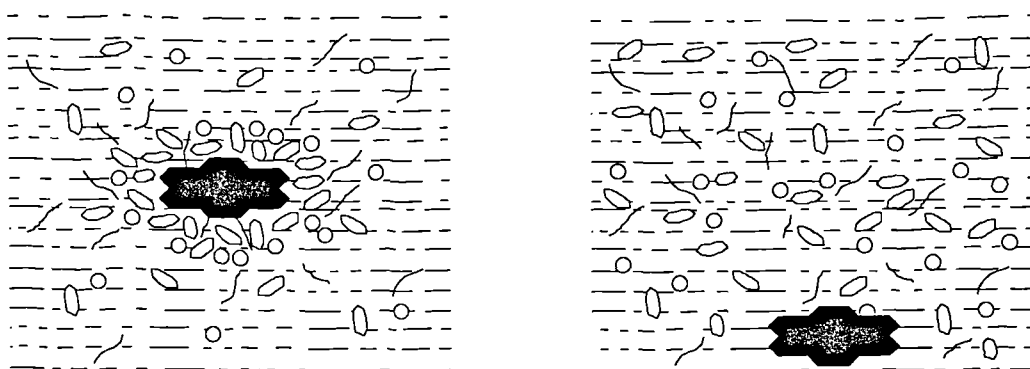


Figure 2-5. Amounts of asphaltenes and resins in crude oils.



(a) Asphaltenes are peptized by resins (after Speight, 1980)

(b) Dilution causes stripping of resins and precipitation of asphaltenes

Figure 2-6. Schematic views of: (a) asphaltene peptized by resins and (b) precipitation when resins are stripped away.

For computational purposes, asphaltenes are usually treated either as true dissolved species (Chung, 1992) or as macromolecules using Flory-Huggins theory (Hirschberg, 1984), neither of which produces a predictive model of asphaltene precipitation. Leontaritis (1989) incorporated the critical resin concentration (CRC) concept (Swanson, 1942), into a thermodynamic model. This is based on the mechanistic concept that below the CRC, resin concentration is too low to coat asphaltene aggregates, therefore precipitation occurs. Steric repulsion has also been suggested, but not yet demonstrated, as a mechanism for asphaltene dispersion (Leontaritis, 1988; Wilhelms and Larter, 1994).

Cimino *et al.* (1996) hypothesize that asphaltenes are lyophilic colloids, solvated by the hydrocarbon medium in which they are dissolved, and have developed a model, based on this premise, that has better predictive capability for the onset of asphaltene precipitation than any reported previously. They argue against any special relationship between resins and asphaltenes because (1) no structure of the sort hypothesized in Fig. 2-6 has ever been observed, (2) asphaltenes are soluble in organic solvents (e.g., toluene), in the absence of any resins, and (3) the resin coating of asphaltenes is not really needed to explain asphaltene phase behavior, as shown by the success of their model. In this view, resins are simply good solvents for the asphaltenes.

Lyophobic colloids are generally viewed as particles of a separate, solid phase, present as a metastable dispersion in the liquid. Lyophilic colloids are in thermodynamic equilibrium with the surrounding solution. There is evidence that asphaltene precipitation is not completely reversible (e.g. Andersen, 1994), but Cimino argues that, as with other macromolecules, the approach to equilibrium may be slow. Experiments of longer duration are required to resolve the reversibility issue.

Solvency of a Crude Oil and the Onset of Asphaltene Precipitation

While the focus of this study is wetting alteration, not asphaltene precipitation *per se*, the effect that the solvent environment has on the state of aggregation of asphaltenes and other polar species may well affect the extent to which wetting alteration is observed. The behavior of polar components at oil/water interfaces, and the possible influence of aggregate size on fluid/solid interactions, will be further investigated in Chapter 3. The onset of asphaltene precipitation is just one point in a spectrum of changing molecular dimensions for the asphaltenes, but it is a useful point since it is readily observed and quantified.

Solubility is the defining characteristic of asphaltenes. Hildebrand's solubility parameter δ , is defined by (Hildebrand and Scott, 1950):

$$\delta = \frac{\Delta E}{V}$$

where ΔE is the heat of vaporization and V is the molar volume. δ has been shown to correlate to the amount of asphaltene precipitated (Mitchell and Speight, 1973) and to the ability of a solvent to dissolve asphaltenes (Burke *et al.* 1990).

Some typical values of δ are plotted in Fig. 2-7a as a function of carbon chain length, for members of several families of homologous compounds. Solubility parameters for mixtures can be calculated if the solubility parameters and mole fractions of each component are known, but for crude oils, such detailed compositional information is rarely, if ever, available. Solubility parameters are strictly applicable to dispersion interactions between nonpolar molecules although the concept has been extended to polar species with terms for polar, acid/base, and hydrogen bonding interactions (Barton, 1991).

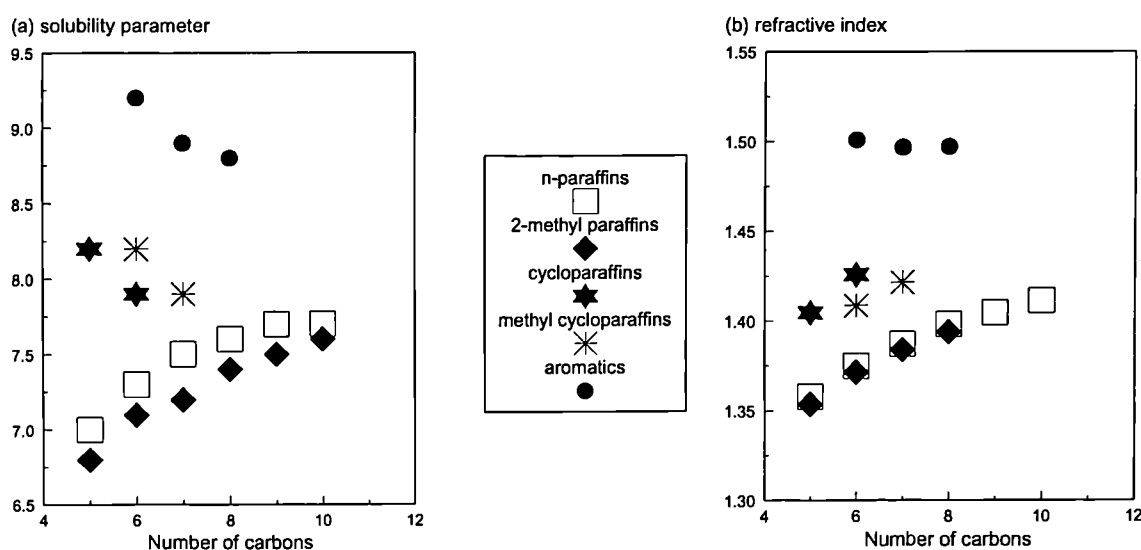


Figure 2-7. Variation of (a) solubility parameters, $\delta(\text{cal/cm}^3)^{1/2}$, and (b) refractive indices of members of several homologous series of hydrocarbons.

Refractive index

Refractive indices (RIs) of the same families of hydrocarbon compounds are shown in Fig. 2-7b. Although there are differences in the details of dependence of RI on carbon chain length and structure, there is an overall similarity between these two parameters, as should be expected, since both arise from polarizability of these nonpolar molecules. Straight and branched chain paraffins have the lowest δ and RI. Both increase with the number of carbons. Aromatics have higher values for both solubility parameter and refractive index; the cycloparaffins are intermediate. Fig. 2-8 shows the nearly linear relationship between solubility parameter and refractive index for a variety of small hydrocarbon species.

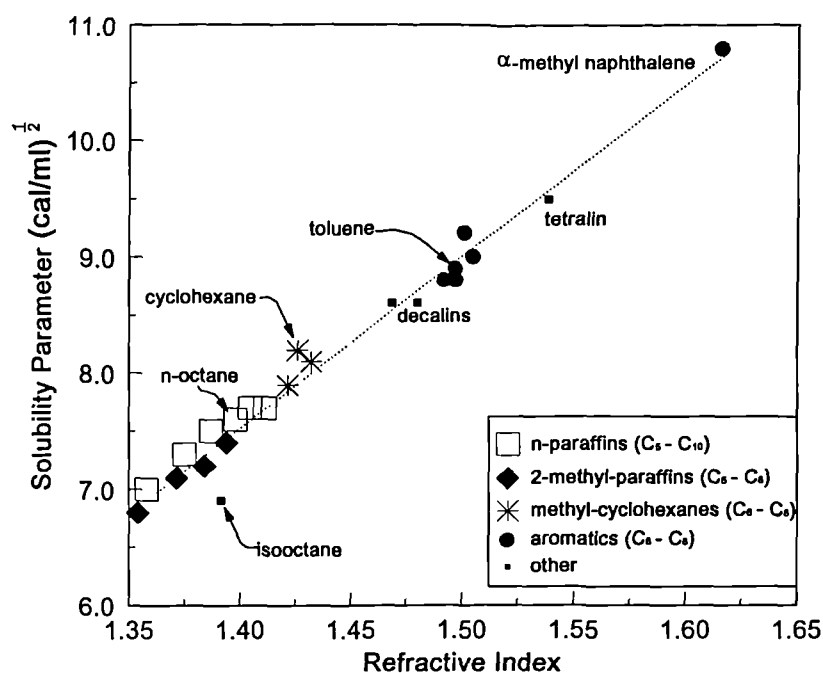
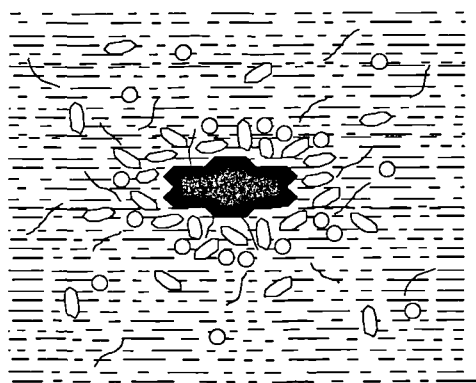


Figure 2-8. Data illustrating the approximately linear relationship between solubility parameter and refractive index for small, nonpolar hydrocarbon molecules.

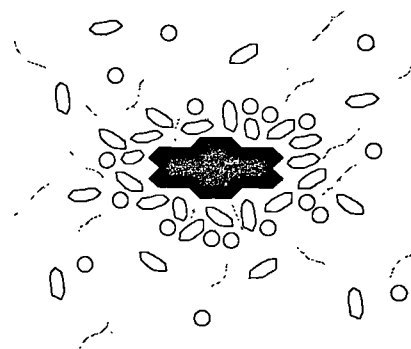
Since RI can be readily determined experimentally for crude oils mixed with solvents and precipitants, it provides a simple measure for characterization of the mixtures used in this study. RIs of crude oils were once commonly measured to distinguish between oils of more paraffinic or more aromatic composition (ASTM D3238-90). Now, however, more detailed chemical methods have become available and RIs are rarely reported. This lack of RI measurements is unfortunate since they provide information about the solvent quality which is an important property, whether the nature of the asphaltenes turns out to be lyophilic or lyophobic.

The lyophilic model uses the difference between solubility parameters of solvent and solute phases as the basis of the Flory interaction parameter. The interaction between lyophobic colloids can be related to the difference in RI between the colloids and suspending medium through relationship of RI to the Hamaker constant (e.g., Israelachvili, 1991). The van der Waals attractive forces between particles suspended in a medium depend on the dielectric constant and RI of that medium. In hydrocarbon media, the Hamaker constant for two particles of one material, separated by another is related to the difference between the

RIs of the two materials. As that difference decreases in absolute value, so, in general, does the Hamaker constant, and thus the magnitude of the van der Waals attractive force. Conversely, dilution of a mixture with a component of contrasting refractive index increases the van der Waals attractive force between colloiddally dispersed particles. As illustrated in Fig. 2-9, precipitation would eventually occur because of the change in solvent refractive index, whether or not there is any change in the hypothetical asphaltene/resin aggregates.



(a) Van der Waals attractive forces between asphaltene aggregates are minimized by high refractive index of the oil.



(b) Dilution changes solvent properties of oil between colloidal asphaltenes and increases the van der Waals attractive forces between them.

Figure 2-9. Interaggregate attractive forces increase as the refractive index of the medium between them decreases and makes them more "visible" to one another.

In either case, the onset of asphaltene precipitation would be independent of both asphaltene and resin concentrations, except as they add to the mixture solvent properties.

Onset of precipitation—microscopic observation

Early studies of asphaltenes included microscopic observations. Preckshot *et al.* (1943) described particles that are "essentially spherical and tend to cluster" on slides with deposited bitumen that were treated with low molecular weight solvents. More recently, Fotland *et al.* (1993) used microscopic inspection to confirm that changes in conductivity, observed as oil is diluted with pentane, correspond to the onset of precipitation. Microscopic observation is a simple but accurate way to observe the onset of precipitation at ambient conditions.

Some experimental details

Crude oil samples from Alaska (A-93), New Mexico (Sulimar Queen) and Wyoming (Schuricht), were used in this study, without filtration, recombination with reservoir gases, or other treatment. Physical properties of the dead crude oil samples used are included in Appendix A. Other chemicals were reagent grade and were used as received. Organic compounds tested included normal- and cyclo-paraffins, olefins, aromatics, and compounds containing polar heteroatoms. Compounds that cause precipitation are distinguished from those that do not. The former are referred to as precipitants and the latter as solvents. These assignments are made with respect to a particular crude oil and may well be different with other crude oils.

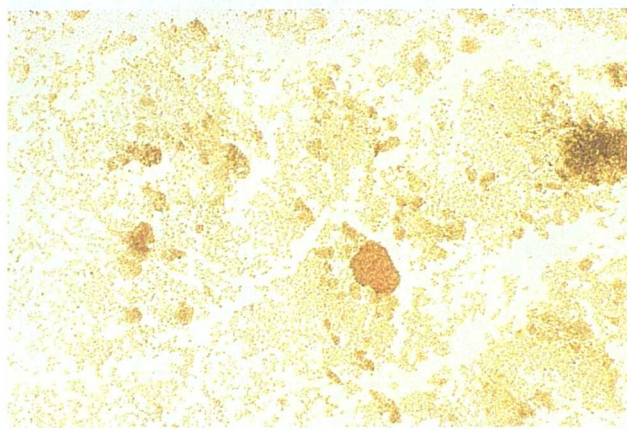
Measured volumes of oil, solvent, and precipitant were mixed in small, capped glass vials. Microscopic observations were made using a Nikon Labophot microscope with transmitted light; RI was measured with an Abbe-3L refractometer. Both measurements were made for each mixture.

At the onset of precipitation, pale structures, of a size that is easily observed under low power, appear in the previously featureless mixture. Clusters of particles that have a spherical appearance become more numerous and more differentiated in color from the liquid medium as greater volumes of precipitant are added to the mixture. Fig. 2-10 shows the appearance of the precipitated asphaltene with an excess of n-pentane added to A-93 crude oil.

Reversibility of precipitation has been observed with volatile precipitants for mixtures near the onset. With time, evaporation of precipitant made the mixture a better asphaltene solvent and all of the precipitated material eventually (over a period of hours or days) disappeared. The precipitation process seemed to be completely reversible.

Crude oils mixed with precipitants

Mixtures of precipitants and A-93 crude oil were prepared in various ratios; some results are shown in Fig. 2-11, where mixture RI is plotted as a function of the volume fraction of crude oil ($f_{V,oil}$). Open symbols indicate mixtures that were free of precipitate. As $f_{V,oil}$ decreases, RI also decreases; eventually precipitate is detected. The highest RI solution that contains precipitate is designated the precipitation onset RI or P_{RI} . Reproducibility is shown in Fig. 2-11a by two tests of precipitation with isooctane, one with microliter quantities and a second using larger (ml) volumes. An arrow marks the P_{RI} mixture.



(a) 4X magnification



(b) 20X magnification

Figure 2-10. Apathenes precipitated from A-93 crude oil with n-pentane(1 volume of oil to 3 volumes of precipitant).

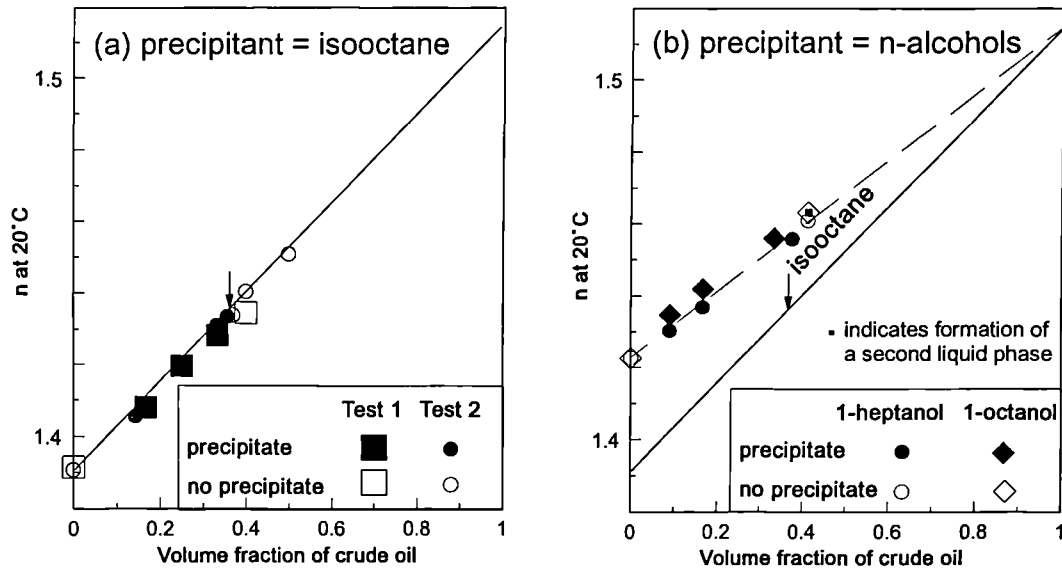


Figure 2-11. Precipitation of asphaltenes from A-93 crude oil mixed with precipitants.

Similar results for mixtures of A-93 with 1-heptanol and 1-octanol are presented in Fig. 2-11b, with the isooctane line included for comparison. Other precipitants tested included many of the normal paraffins from pentane through pentadecane and two mineral oils, Soltrol 130 and 220. The data, summarized in Table 2-1, show that the onset of precipitation occurs over a fairly wide range of refractive index values for different precipitants. Tests conducted with n-pentane and n-hexane were less repeatable than those with other precipitants, probably because of the volatility of pentane at ambient conditions. Table 2-2 compares the results of precipitation induced by isooctane for four different crude oils.

Mixtures of crude oil, precipitant, and solvents

Addition of solvent changes the amount of precipitant that must be added to initiate precipitation. The minimum amounts of isooctane required to initiate precipitation from A-93 and from mixtures of A-93 with several nonpolar hydrocarbon solvents are shown in Fig. 2-12a. Toluene is less effective than the oil itself in preventing precipitation so the volume fraction of isooctane required to initiate precipitation ($f_{V,pp}$) of a mixture of oil and toluene is a little less than for the undiluted oil. α -Methylnaphthalene is a better solvent for the asphaltenes than the crude oil so more isooctane is required to initiate precipitation from mixtures that include α -methylnaphthalene. Several polar solvents were also tested. As shown in Fig. 2-12b, these polar compounds are also better solvents than the oil itself.

Table 2-1. Onset of precipitation from A-93 crude oil with different precipitants at ambient conditions.			
Precipitant	$n_D^{20 r}$	Onset of precipitation:	
		$f_{V,ppt}$	$n_D^{20 m}$
isooctane	1.3915	0.643	1.4335
isooctane [*]	"	0.670	1.4282
n-pentane	1.3580	0.600	1.4468
n-hexane	1.3749	0.583	1.4404
n-heptane	1.3870	0.600	1.4385
n-octane	1.3980	0.583	1.4460
n-nonane	1.4045	0.583	1.4505
n-decane	1.4113	0.615	1.4505
n-dodecane	1.4216	0.625	1.4566
n-tridecane	1.4256	0.625	1.4582
n-tetradecane	1.4290	0.667	1.4560
n-pentadecane	1.4315	0.588	1.4650
Soltrol 130	1.4235 ^m	0.677	1.4541
Soltrol 220	1.4357 ^m	0.688	1.4605
1-heptanol	1.4249	0.625	1.4560
1-octanol	1.4295	0.667	1.4562

^r reference values (from CRC or Aldrich catalog)

^m measured values

^{*} experiment repeated with larger volumes of oil and precipitant

Table 2-2. Onset of precipitation from different crude oils mixed with isooctane.		
Crude Oil	$f_{V,ppt}$	P_{RI}
A-93	0.643	1.4335
Moutray	0.583	1.4388
Schuricht	0.524	1.4535
Sulimar Queen	0.615	1.4330

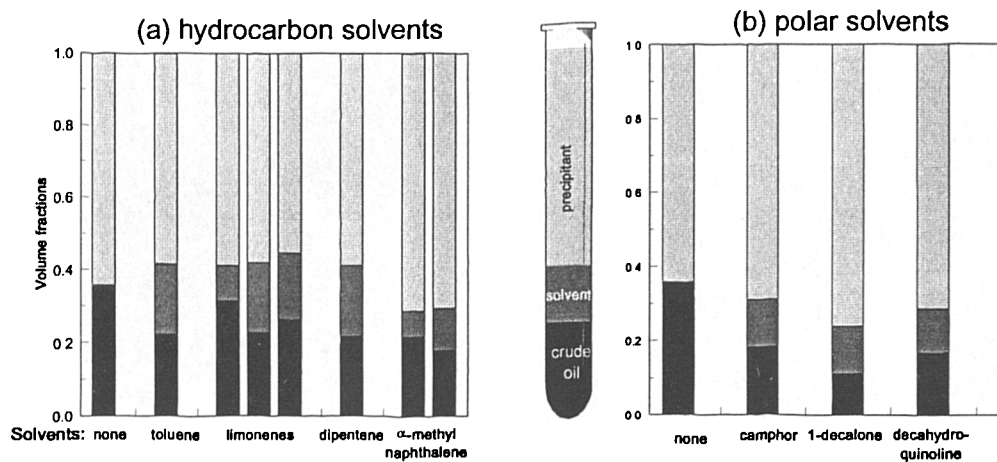


Figure 2-12. Volume fraction of isooctane required to initiate precipitation from A-93 mixed with hydrocarbon and polar solvents.

The conditions at the onset of precipitation, with and without added toluene are compared for three precipitants and A-93 in Table 2-3. P_{RI} ranges from a low of 1.4335 for isooctane to a high of 1.4605 for Soltrol 220. For a particular precipitant, addition of toluene changes $f_{V,ppt}$ but has much less effect on P_{RI} .

Table 2-3. Onset of precipitation from A-93 crude oil with mixtures of precipitants and toluene at ambient conditions.				
Precipitant	Solvent	Volume fractions (f_v):		P_{RI}
		Precipitant	Solvent	
1-heptanol	no solvent	0.625	—	1.4560
	toluene	0.6	0.2	1.4550
		0.455	0.045	1.4690
Soltrol 220	no solvent	0.688	—	1.4605
	toluene	0.662	0.11	1.4597
isooctane	no solvent	0.643	—	1.4335
	toluene	0.583	0.194	1.4398
		0.643	0.107	1.4355

Fig. 2-13 summarizes the observations of P_{RI} for A-93 and different precipitants, with and without added solvents. The horizontal band shades the narrow range of RI values in

which most of the conditions for onset of precipitation with isooctane alone and with hydrocarbon solvents are found. Values of $f_{V,oil}$ vary widely as the oil is diluted with different solvents, but P_{RI} is remarkably constant. α -Methylnaphthalene, for example, contributes to the stability of mixtures in proportion to its high RI. Other hydrocarbon solvents reduced the mixture RI and thus the amount of isooctane required to reach P_{RI} .

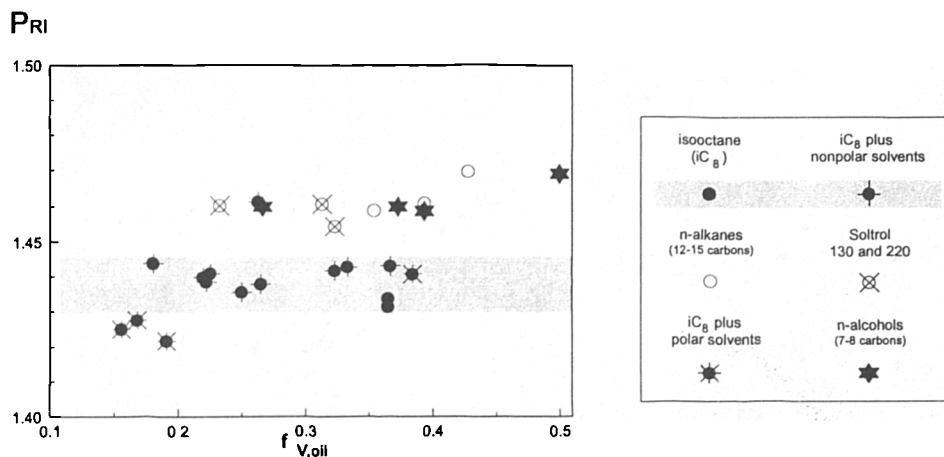


Figure 2-13. P_{RI} (the refractive index at the onset of asphaltene precipitation) as a function of the volume fraction of A-93 crude oil.

Onset of asphaltene precipitation from mixtures of constant RI

A number of studies in the literature have examined the onset of asphaltene precipitation from mixed solvents. Many of these have noted a linear relationship between volumes of solvent and precipitant in mixtures where precipitation is first noted (Heithaus, 1962; Bichard, 1969; Waxman *et al.*, 1980; Hotier and Robin, 1983; Reichert *et al.*, 1986; Cimino *et al.*, 1996).

These relationships can be reexamined in the context of the P_{RI} concept. The amounts of solvent, precipitant, and oil (or tar, residue, etc.) have been combined in various ways to characterize (1) the solvent quality of the mixture and (2) the dispersability of the asphaltenes. Waxman's

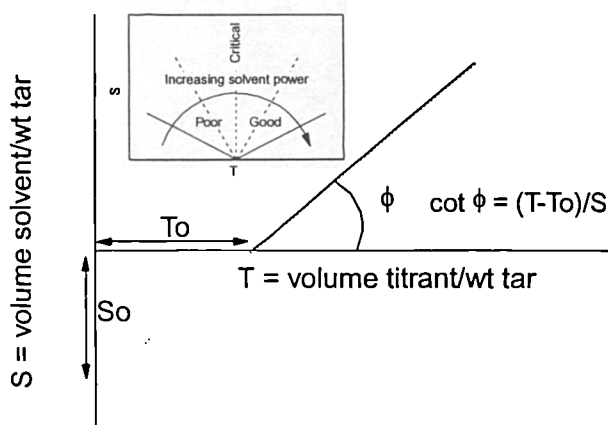


Figure 2-14. Precipitation of asphaltenes from tars mixed with titrant (precipitant) and solvent (from Waxman *et al.*, 1980). Ratio of S to T is linear and $\cot \phi$ is an indicator of solvent power.

version is typical. The volumes of solvent and precipitant (or titrant) at the onset of precipitation from Peace River and other tars were plotted against one another, as shown schematically in Fig. 2-14. Two parameters characterize each tar/solvent/precipitant combination: the minimum amount of precipitant required when no solvent is present (T_o), and the solvent quality which is related to $\cot \phi$ (the symbols are defined in Fig. 2-14). T_o is characteristic of the sample of tar and the precipitant, whereas $\cot \phi$ is characteristic of the tar sample and the solvent.

Oil represents a significant fraction of each of the mixtures in Table 2-3, whereas most investigators have used volumes of solvent and precipitant that are much larger than the amount of oil. In order to see a linear relationship, the contribution of oil to the properties of the mixture must be small. Heithaus (1962) defined a flocculation ratio ($FR = V_p/(V_p+V_s)$) where V is volume and the subscripts p and s refer to precipitant and solvent, respectively) and observed that FR approaches a maximum value as V_p and V_s increase. FR_{max} can be related to Waxman's results by a simple formula: $\cot \phi = (1-FR_{max})/FR_{max}$.

Most of the titration data reported in the literature are for dilute systems where $FR \approx FR_{max}$. In this region, mixture RI is constant and can be calculated for the binary mixture of solvent and precipitant, ignoring the small contribution from the oil. Thus values of P_{RI} can be estimated from published data relating volumes of various solvents and precipitants at the onset of precipitation. For example, Cimino *et al.* (1996) report precipitation titrations with n-pentane from a very light crude oil (less than 1% asphaltenes) with the solvents toluene and tetralin.

We can estimate the refractive index of an ideal mixture by combining the molar polarizations of the pure components on a mole fraction basis. The equation of Clausius-Mossotti (e.g., Shoemaker *et al.*, 1989) defines the molar polarization of a pure substance:

$$P_M = \frac{\epsilon - 1}{\epsilon + 2} \frac{M}{\rho} \quad [2-1]$$

where: P_M = molar polarization

ϵ = dielectric constant

M = molecular weight

ρ = density

The molar polarization can be expressed as the sum of two contributing parts, the distortion polarization P_d , and the orientation polarization P_μ . For hydrocarbons, the orientation contribution is minimal and $P_M \approx P_d$. P_d can be expressed by the equation of Lorentz and Lorenz for the molar refraction, in terms of the refractive index, n :

$$R_M = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{\rho} = P_d \quad [2-2]$$

Thus, for a binary mixture:

$$P_M = X_1 P_{1M} + X_2 P_{2M} \approx X_1 R_{1M} + X_2 R_{2M} \quad [2-3]$$

where X = mole fraction

This approximation can break down either because of non-ideality of the mixture or because of significant orientation polarizations. For pure components, the mixture properties can be measured.

Using Cimino's data and the molecular properties in Table 2-4, values of P_{RI}^* can be estimated, as shown. Toluene and tetralin have very different physical properties, but the calculated values of P_{RI}^* are quite similar.

Table 2-4. Calculation of P_{RI}^* (data of Cimino <i>et al.</i> , 1996).			
	n-pentane	toluene	tetralin
M	72.15	92.14	132.21
ρ	0.6262	0.8669	0.9702
n_D^{20}	1.3579	1.4961	1.5413
precipitating mixture	201 g	296 g	
	240 g		258 g
P_{RI}^*		1.43	1.42

P_{RI} for n-paraffins of varying carbon chain length

P_{RI} is approximately constant for a given precipitant with various solvents, but its value varies for different precipitants (Tables 2-1 and 2-3). Fig. 2-15 shows P_{RI} measured for A-93 with C_5 to C_{15} n-paraffins and several different solvents. P_{RI} values in different solvents are in good agreement for carbon chain lengths of 7 and above, but there is much more scatter for n-pentane and n-hexane. The volatility of the low molecular weight hydrocarbons is probably the main limitation for these tests at ambient conditions. As the molecular weight of precipitant increases, so does the corresponding P_{RI} .

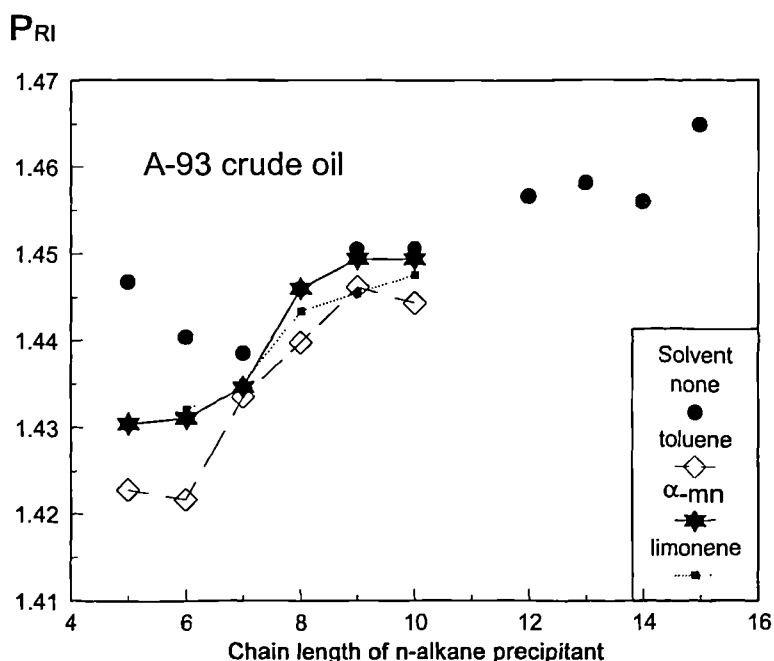


Figure 2-15. P_{RI} for n-alkane precipitants and A-93 crude oil.

Hotier and Robin (1983) reported titration data, similar to Waxman's. For one sample they reported 33 combinations of 10 solvents and 6 precipitants. P_{RI}^* values have been calculated for many of these mixtures (Fig 2-16). The trend of increasing P_{RI}^* with increasing molecular weight is very similar to that shown in Fig. 2-15 for A-93. C_{30} is squalane, a branched alkane that is not strictly comparable, but the other precipitants are n-alkanes. Mixtures with tetralin may not be ideal.

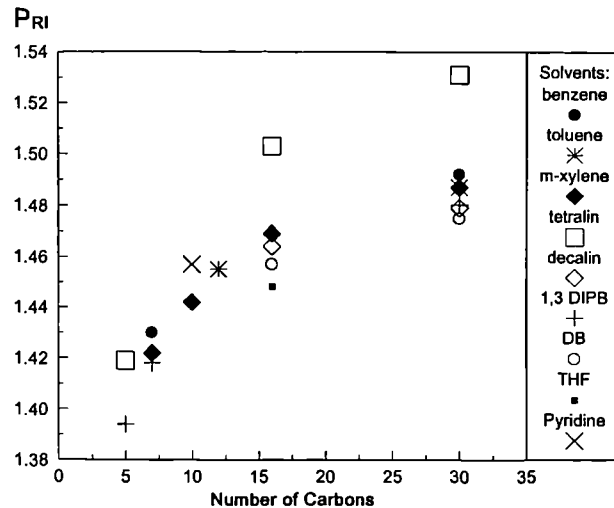


Figure 2-16. P_{RI} for n-alkane precipitants and various solvents calculated from the data of Hotier and Robin (1983), Figure 17.

Comparison of the results in both Figs. 2-15 and 2-16 with the predictions of Cimino *et al.* (1996) lends support to their hypothesis that asphaltene precipitation can be modeled thermodynamically by treating the asphaltenes as lyophilic colloids. The P_{RI} method provides a very simple way to quantify the onset of asphaltene precipitation and, perhaps even more importantly, to describe the solvent quality. Since aggregation of the polar components is affected by solvent quality, their tendency to alter wetting may be affected as well, a possibility that will be considered further in Chapter 3. While solvent quality alone does not determine the outcome of exposure of rock surfaces to crude oil, it is one of the factors that may well be involved in alteration of wetting of crude oil/brine/rock ensembles.

Summary

This chapter has provided background on crude oil composition that will be needed to evaluate results of some of the COBR wettability studies in the remainder of the thesis. An important concept, the ability of the oil to act as a solvent for its asphaltenes, has been examined in detail.

High molecular polar compounds found in most crude oils are capable of interacting with mineral surfaces to alter their wetting. While the amount of these materials present in a given crude oil has never been shown definitively to correlate with the extent of wetting alteration by that oil, their presence is certainly a necessary condition for the crude oil/brine/rock interactions that determine reservoir wetting conditions. Some of the

differences between crude oils that may help to account for their varying propensities to alter wetting include:

1. The amount of the polar functionality (and the amount that can act as either acidic or basic sites and thus affect charge density at the oil/water interface) is an important characteristic of the asphaltene and resin fractions of each crude oil. The chemical nature of the asphaltene components that may contribute to acid/base interactions was introduced in this chapter. We will return to these acid/base interactions and their importance in wettability alteration of crude oil/brine/rock ensembles in Chapter 3.
2. The molecular weights and extent of aggregation of the asphaltene fraction may well affect their partitioning and exchange rates between oil/water interfaces and bulk oil.
3. A key question, that has been addressed at some length in this chapter is: How good a solvent is a given crude oil for its asphaltenes? This point is important because of the demonstrated effect of solvent quality on aggregate size. Thus all of the molecular species in a crude oil, contributing to the solvent properties of that oil, can affect how the high molecular weight, polar species interact among themselves and, ultimately, with brine and solid surfaces.

In this chapter, dealing primarily with components of crude oils, we have concentrated on observations of the onset of asphaltene precipitation. The onset of precipitation gives one fixed point in the spectrum of changes in the aggregate size of the asphaltenes. A simple method, using mixture refractive index to quantify solvent quality has been demonstrated. It has further been shown that many of the reports in the literature of a constant ratio of solvent to precipitant in precipitating mixtures is a manifestation of our observation that there is a constant value of RI at which precipitation is first observed for a given oil and precipitant. In the limit of large dilution, where the oil itself contributes little to the mixture refractive index, this ratio fixes the value of P_{RI} . Thus values of P_{RI} for a variety of oils, precipitants, and solvents can be estimated from previously published data.

Oil solvent properties are relevant to investigations of COBR wetting because the interfacial activity of the high molecular weight components most responsible for COBR interactions may be changing in response to changes in their solvent environment. The tendency for specific oil components to alter wetting may differ from one crude oil to another if the solvent environments are not the same.

Connate water is always present in oil reservoirs; additional water is often introduced during production, either as natural aquifer drive or as injected water. Both connate and invading water contain varying amounts of salts. Interactions between crude oil components and these brines can influence wettability. The roles of brine in bulk and in thin films, including the properties of oil/brine interfaces, oil/brine/solid interactions and their contributions to wetting will be considered in this chapter.

Why Does Water Influence Wettability?

In all likelihood, most reservoir rocks are strongly water-wet before the invasion of crude oil. Oil invades as the nonwetting phase with the consequent distribution of water in the smallest pore spaces and oil in larger pores. The presence of water is responsible for this initial distribution of fluids. This is water's first important role in determining the complex mixtures of wetting conditions that can develop in rocks filled with crude oil and brine.

Wettability changes as surface active components from the crude oil adsorb on the mineral surfaces. This surface active material is unusual in several respects:

- the molecules and/or aggregates are very large,
- chemically, these molecules are mostly hydrocarbon, with minor polar functionality,
- water solubility is very low, and
- solubility in oil is also limited.

This unusual combination of chemical characteristics results in a material that is mainly adsorbed neither from water solution nor from oil, but from the oil/water interface.

With adsorption occurring from the oil/water interface, the composition of the water phase is very important in how wettability evolves. Both the solid/water and oil/water interfaces have ionizable sites. Charging of these discrete sites and net charge of the interfaces both depend on brine composition, as reflected in such interfacial properties as interfacial tension and electrophoretic mobility. Ultimately, adsorption and wettability alteration also depend on these charged interfacial species.

The Oil/Water Interface

Electrophoresis of emulsified droplets of crude oil in brines of varying composition demonstrates that crude oil interfaces have net positive charge at low pH and net negative charge at high pH (Buckley *et al.*, 1989; Dubey and Doe, 1993). Fig. 3-1 shows measured zeta potentials for Moutray crude oil, emulsified in NaCl brines, with concentrations from 0.001 to 0.1 M and pH from about 2 to 10.

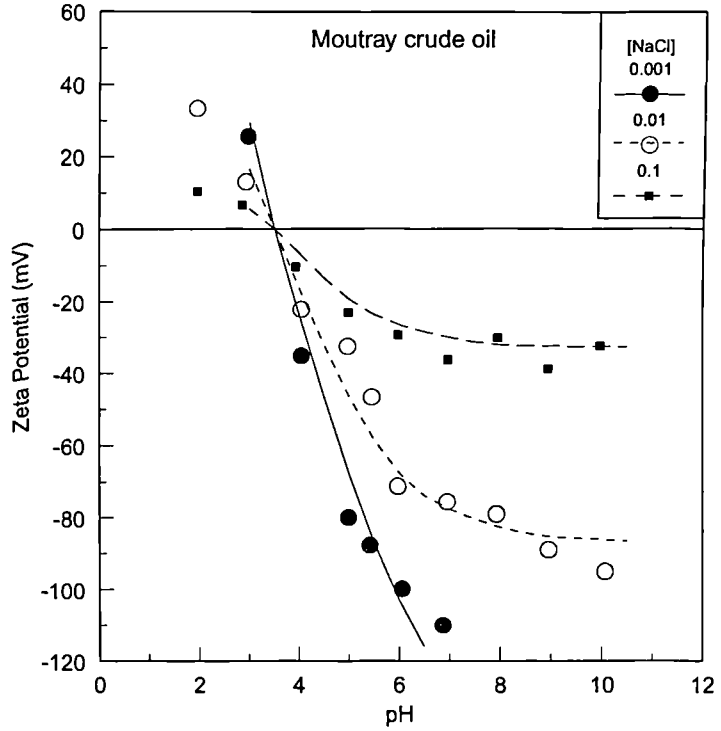


Figure 3-1. Zeta potentials of emulsions of Moutray crude oil in brines of varying pH and ionic strength. (after Buckley *et al.*, 1989)

Dissociation of organic acids and bases at the oil/brine interface provides an explanation that is consistent with the observed zeta potential measurements. Using the Ionizable Site Group (ISG) model (Healy and White, 1978; Takamura and Chow, 1985), and assuming organic acids and bases with surface density and pK_a values shown in Table 3-1, the observed zeta potentials could be matched for all of the brine conditions, as shown by the lines in Fig. 3-1 (Buckley *et al.*, 1989). Additional details of calculations of surface charge and zeta potential are provided in Appendix C.

Table 3-1. Ionizable surface group model parameters.				
Crude Oil	Acidic sites		Basic sites	
	$N_a(\text{acid})$ (number/m ²)	$pK_a(\text{acid})$	$N_a(\text{base})$ (number/m ²)	$pK_a(\text{base})$
Moutray	$0.4 \cdot 10^{18}$	4	$0.1 \cdot 10^{18}$	6
ST-86	$2.0 \cdot 10^{18}$	1.75	$2.08 \cdot 10^{18}$	5.8

Changes in interfacial tension (IFT) with pH provides another indication that both acids and bases are active at crude oil/brine interfaces (Reisberg and Doscher, 1956; Cratin, 1969; Trujillo, 1983). Fig. 3-2 from Reisberg and Doscher (1956) and Fig. 3-3 with data for A-93 crude oil both show that IFT is highest near neutral pH and decreases as pH is either increased or decreased. Fig. 3-3 shows, in addition, that the total ionic strength of the brine solution influences the shape of the IFT vs pH relationship, as it does the electrophoretic mobility. The ISG model can be used to describe oil/brine interfaces with surface charge vs pH relationships of very similar shape to the IFT curves, as will be shown first for solutions of known acids and bases, then for crude oils.

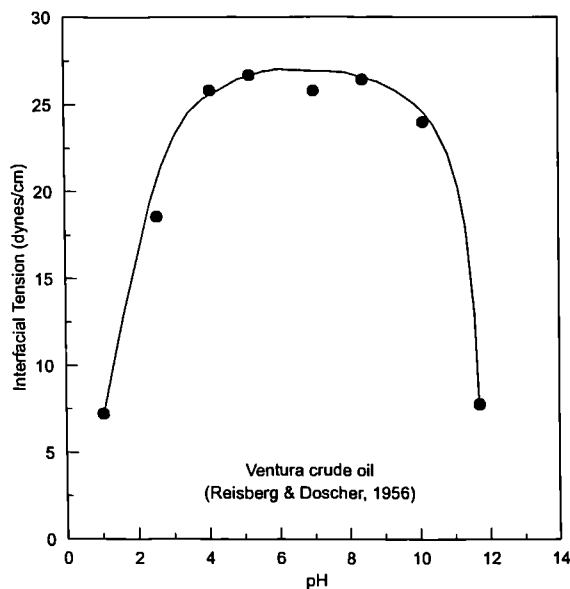


Figure 3-2. IFT between Ventura crude oil and brines of varying pH shows the characteristic drop in tension at both high and low pH.

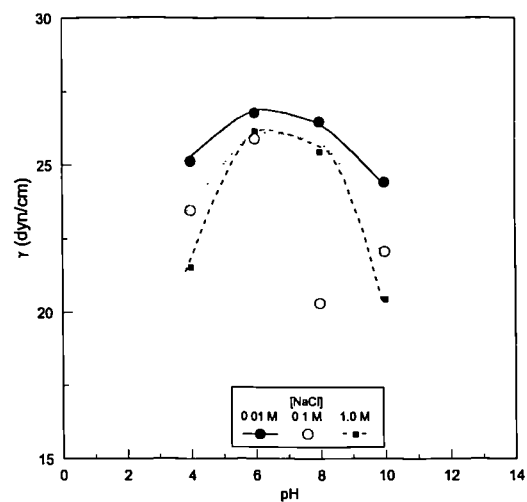


Figure 3-3. IFT between A-93 crude oil and brines of varying pH and ionic strength.

Tests of the ISG model with organic acids and bases

IFTs measured between oil solutions of water-insoluble fatty acids and aqueous solutions of varying pH have been reported, showing that IFT decreases with increasing pH (Hartridge and Peters, 1922; Peters, 1931; Danielli, 1937; Cratin, 1993). The data reported by Danielli for oleic acid (cis-9-octadecenoic acid, $C_8H_{17}CH=CH(CH_2)_7COOH$) are shown in Fig. 3-4. A titration curve for an acid with a pK_a of 7.5 is shown for comparison (the scale is normalized charge, from 0 to -1). The drop in IFT corresponds roughly to dissociation of the acidic functional groups with increasing pH. A pK_a of 7.5 is, however, higher than expected; water-soluble carboxylic acids have pK_a values closer to 5.

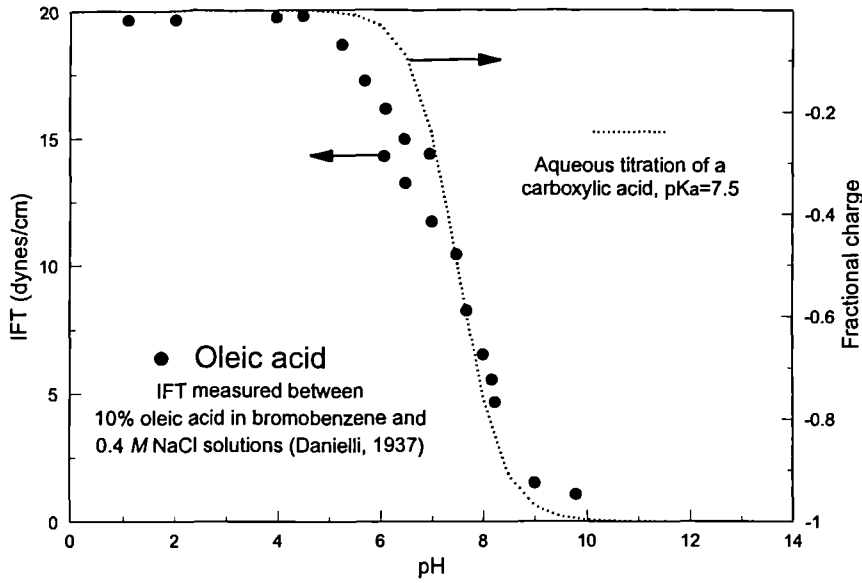


Figure 3-4. IFT between 0.4 M NaCl and bromobenzene solutions of oleic acid is shown on the left axis. On the right is the calculated charged fraction of an aqueous solution of a weak acid ($pK_a = 7.5$). Both change with solution pH.

Fig. 3-5 shows an even greater shift in apparent pK_a for stearic acid (octadecanoic acid, $C_{17}H_{33}COOH$) reported by Cratin. An aqueous acid would have to have a pK_a of 10.5 to give a comparable titration curve.

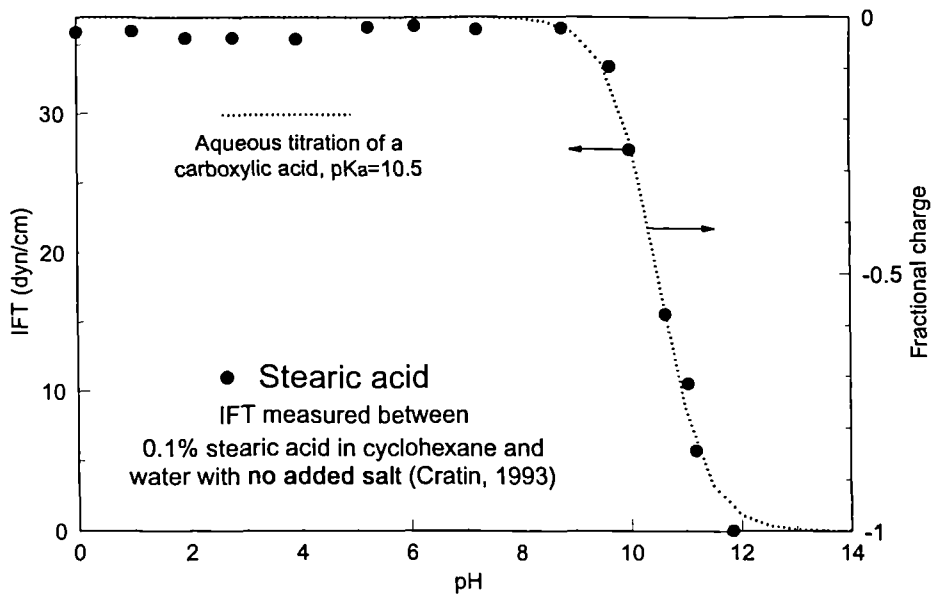


Figure 3-5. IFT between stearic acid solutions and distilled water with HCl or NaOH added to adjust the pH is shown on the left axis. The calculated fractional charge is shown to the right for titration of a weak acid ($pK_a = 10.5$).

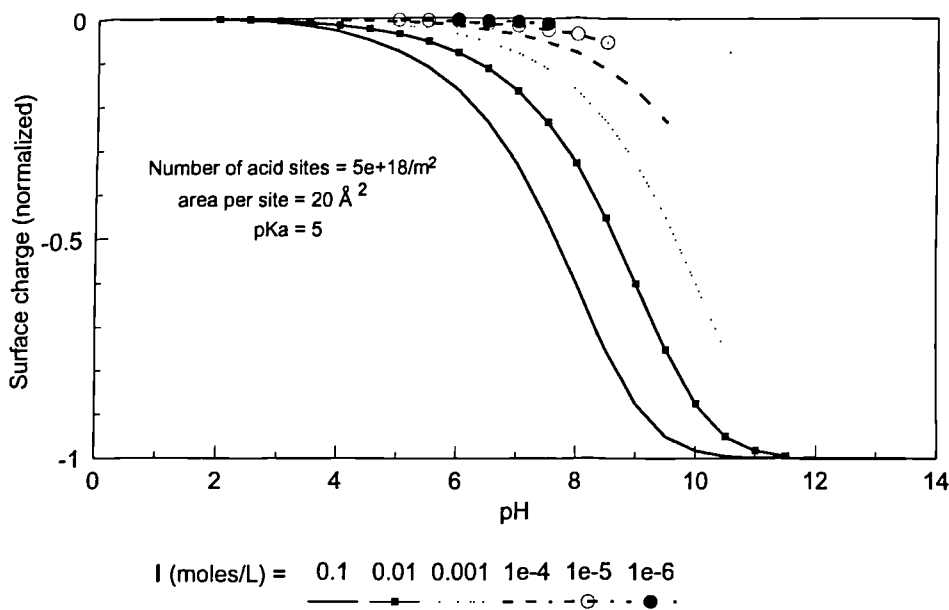


Figure 3-6. Calculated surface charge for a hypothetical surface made up of ionizable sites. Surface charge depends on the site density and pK_a of the ionizable sites (taken here to be $5 \cdot 10^{18}/m^2$ and 5 respectively), together with aqueous phase pH and ionic composition, as shown.

Rather than postulate a shift in pK_a , for whatever reason, Gouy-Chapman theory can be used to calculate the concentrations of ions near an oil/brine interface with a given density of charged sites. The interfacial charging mechanism is assumed to be dissociation of acidic (and/or association of basic) sites, with some density of chargeable sites (N_a , m^{-2}) and a dissociation constant, K_a . Hydrogen ion concentrations are key to determination of dissociation, but other ions in solution influence these concentrations and thus the variation of surface charge with pH. Fig. 3-6 shows the calculated surface charge for a hypothetical acidic oil interface ($N_a = 5 \times 10^{18}/m^2$ and $pK_a = 5$) as a function of pH in contact with aqueous solutions of constant ionic strength. Increasing ionic strength shifts the dissociation to lower pHs, toward the aqueous titration curve.

Two examples of ISG calculations are shown in Figs. 3-7. Surface charge is plotted on the right axis and the measured IFT data are plotted with respect to the left. Fig 3-7a shows the data and calculated surface charge for oleic acid with 0.4 M buffers. Calculations and data for stearic acid with no added salts in the aqueous phase are shown in Fig 3-7b.

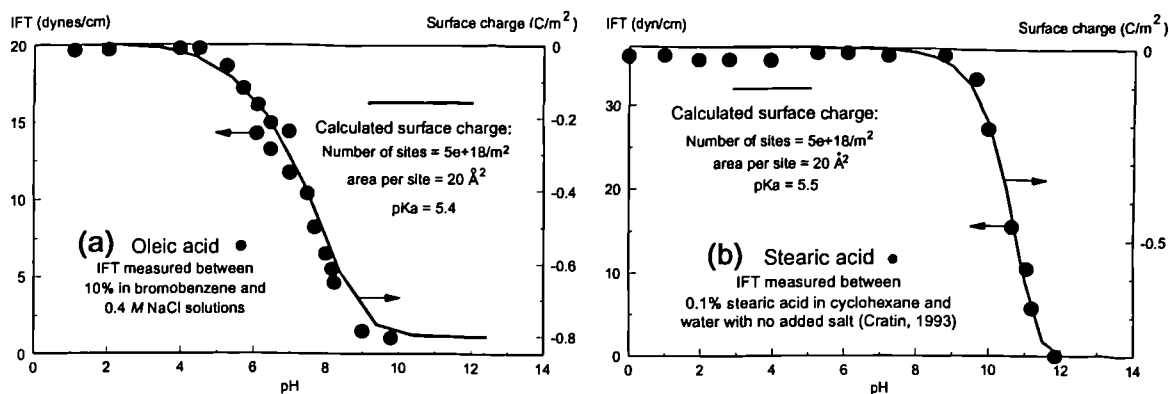


Figure 3-7. IFT response for two oil-soluble acids correlates with surface charge for a reasonable density of weakly acidic ionizable sites, with pK_a values that are typical of carboxylic acids in aqueous solution, as shown for (a) oleic acid and (b) stearic acid.

The ISG model parameters that gave surface charge curves of the same shapes as the measured IFT data are very similar. Both had $N_a = 5 \cdot 10^{18}$ carboxylic acid sites/ m^2 of oil/brine interface, corresponding to a maximum area per charge of 20 \AA^2 . pK_a values of 5.4 for oleic acid and 5.5 for stearic acid are only slightly higher than those measured for water soluble organic acids. Table D-1 (Appendix D) shows the pK_a of acetic acid is 4.75 and that pK_a increases with carbon chain length up to n-nonanic acid ($pK_a=4.96$) so the values of 5.4 and 5.5 for these two 18 carbon acids are reasonable. The value of 20 \AA^2 for the surface area per carboxylic acid site is the so called Pockels point, and is very close to Langmuir's subsequent measurements of 21 \AA^2 for palmitic ($C_{15}H_{31}COOH$), stearic, and cerotic ($C_{25}H_{51}COOH$) acids spread at an oil/water interface (Adamson, 1990).

Interfaces that acquire a positive charge because of association between basic species and protons also show lower IFT as extent of charge increases, and shifts of apparent pK_a consistent with the ISG model, as shown in Fig. 3-8 for hexadecylamine. The pK_a of 10.65 is about that of laurel amine ($C_{12}H_{25}NH_2$); the area per site was adjusted to get the best correspondence between surface charge and IFT. The resulting value of 7 \AA^2 seems low and has not yet been confirmed.

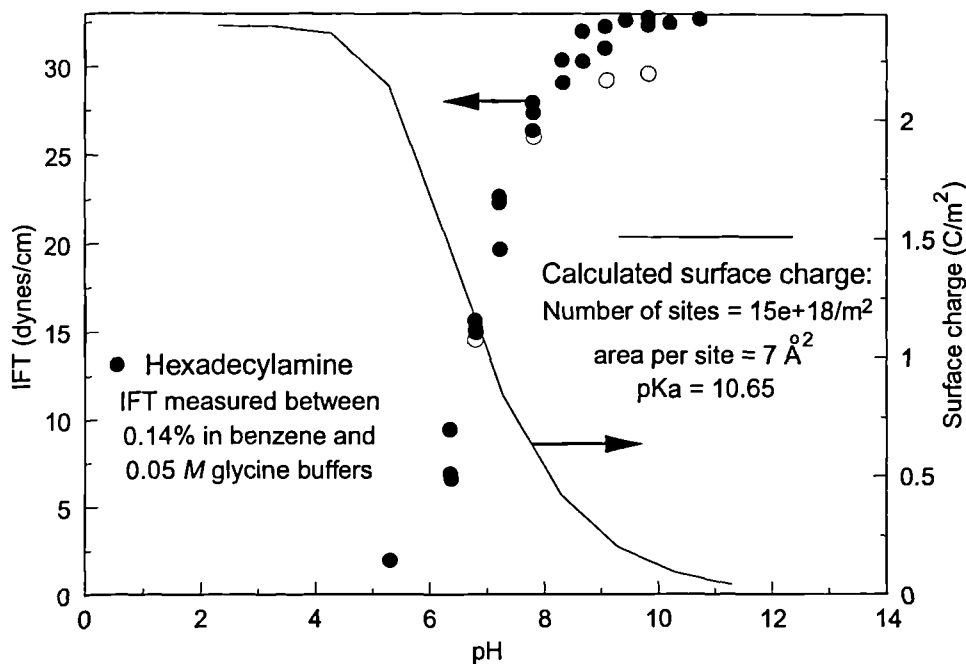


Figure 3-8. IFT between hexadecylamine solutions in benzene and aqueous buffers correlates with the extent of charge of the positively charged amine surface. (IFT data from Peters, 1931)

Contact angles on an acidic solid surface

Advancing contact angles (θ_A) between water and air have been shown to be pH-dependent on carboxylic acid-substituted polyethylene surfaces (Holmes-Farley *et al.*, 1985; Whitesides, 1991). The shift in apparent pK_a in the θ_A vs pH curve is reminiscent of fatty acid/water IFT measurements, with similar confusion regarding the impact of changing ionic strength. An interphase region with varying dielectric properties grading from polyethylene (~ 2) to water (~ 80) and polyacidic interactions, in which ionization of one site alters the properties of adjacent sites, are cited as explanations for K_a shifts of two to four orders of magnitude. Fig. 3-9 shows ISG model calculations compared to some of the contact angle data. The carboxylic acid functions fixed at a solid/water interface behave very similarly to those at the oil/water interface; good comparisons were obtained with $pK_a=5.25$ and 20 \AA^2 per site. Remarkably, contact angle measurements reflect the pH and ionic strength dependence almost as well as IFT.

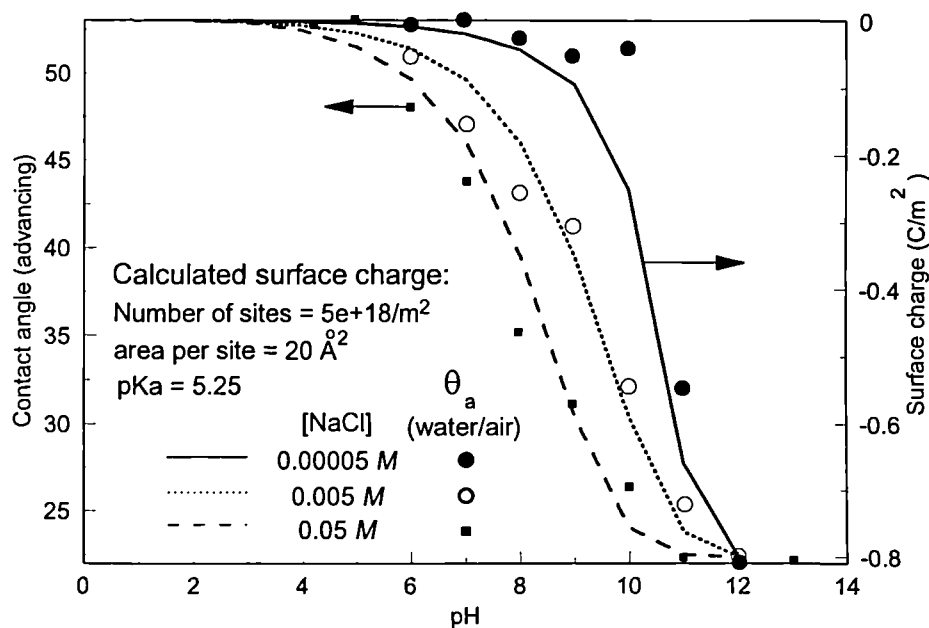
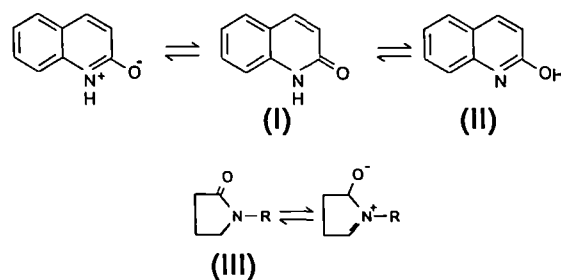


Figure 3-9. Contact angles on functionalized polyethylene surfaces appear to be related to surface charge. (contact angle data from Holmes-Farley *et al.*, 1985)

Interfaces with both acidic and basic functional groups

Polar functional groups in crude oils: Functional groups that contain either nitrogen or oxygen or both provide basic, acidic, or even zwitterionic character at the oil/water interface. Dissociation constants of selected analogs of the polar functional groups with acidic and/or basic character are included in Appendix D (Tables D-1 through D-3). pK_a changes only slightly with alkyl substitution. Aryl substitution of amines and incorporation of nitrogen into heterocyclic rings has a greater effect on dissociation, resulting in weakly basic functional groups.

Amphoteric compounds, for example the 2-quinolone illustrated (I), have been reported in crude oils (Petersen, 1986; Branthaver *et al.*, 1992). These cyclic amides can also exist in the tautomeric form 2-hydroxyquinoline (II). N-alkylpyrrolidones (III), based on 5-membered rings, have been reported to have surface active properties and to exist, at least partially, as their zwitterionic equivalents (Rosen *et al.*, 1988), although they



have not as yet been identified in crude oils. A much broader range of pK values is possible with zwitterionic species than with the most likely acidic and basic compounds.

As discussed in Chapter 2, the large, polar substituted molecules in the asphaltene fraction have very high molecular weights. The ratio of elements on average can be represented by the empirical formula $C_{100}H_{115}N_1S_3O_2$. The hydrogen to carbon ratio indicates a high degree of aromaticity. Nitrogen content varies only a little, while oxygen and sulfur are more variable. These molecules are predominantly hydrocarbon; the polar substituents are probably not sufficient to confer significant water solubility, but the extent of polar functionality may well contribute to the affinity of these molecules for the oil/brine interface.

Surface charge as a function of brine pH: Many crude oils have both acidic and basic ionizable sites at the oil/water interface (Buckley *et al.*, 1989; Dubey and Doe, 1993). As two interfaces approach one another, the electrostatic forces between them will vary with net charge, but as separation distance decreases the existence of discrete sites of positive and negative charge becomes increasingly important. If we make the simplifying assumption that all the acids can be assigned one value of $pK_a(\text{acid})$ and the bases a value of $pK_a(\text{base})$, the extent to which acidic and basic sites are ionized at the oil/water interface depends, on:

- the aqueous solution composition (pH, I)
- ISG model parameters: $pK_a(\text{acid})$, $N_a(\text{acid})$; $pK_a(\text{base})$, $N_a(\text{base})$, and
- the relative numbers of acidic and basic sites.

With this level of complexity, it is not immediately obvious what the state of charge of such an interface will be. Nevertheless, calculations can be made, assuming some reasonable values for the ISG parameters to show how interfacial charge changes with pH and ionic composition of the water phase.

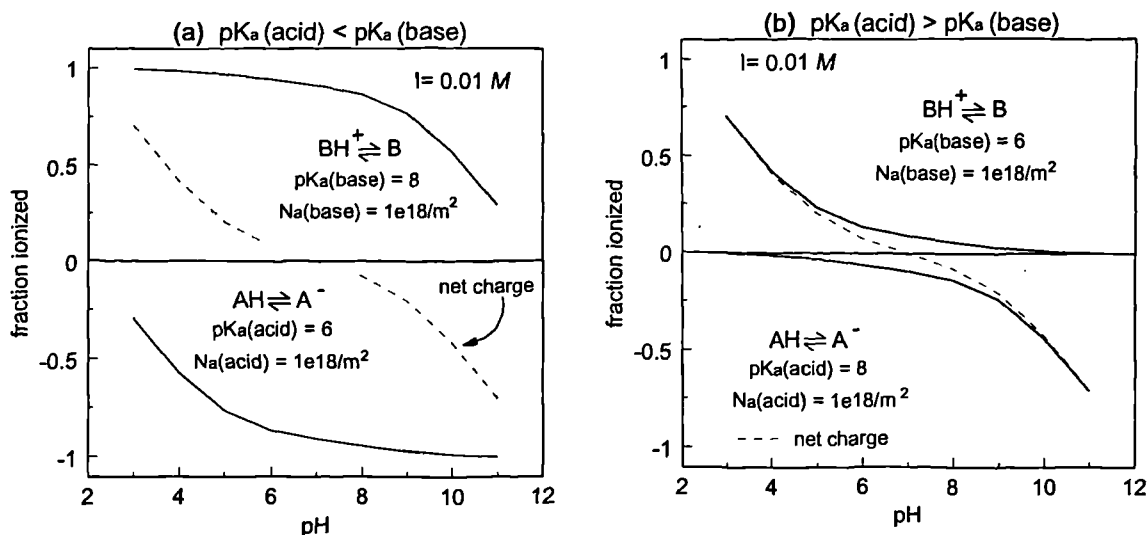


Figure 3-10. Calculated surface charge for hypothetical zwitterionic surfaces with equal numbers of acidic and basic sites and (a) $pK_a(\text{acid}) < pK_a(\text{base})$ or (b) $pK_a(\text{acid}) > pK_a(\text{base})$.

A simple illustration of the results of calculations of interfacial charge is shown in Fig. 3-10 for two quite different surfaces, both of which would have the same zeta potential. Both have equal numbers of acidic and basic sites ($1 \cdot 10^{18}$ of each), pK_a values of 6 and 8, and low salinity ($I = 0.01 M \text{ NaCl}$). If $pK_a(\text{acid})$ is less than $pK_a(\text{base})$ as shown in Fig. 3-10a, both acidic and basic species are ionized over a wide pH range. In the opposite case where $pK_a(\text{acid}) > pK_a(\text{base})$, as in Fig. 3-10b, the extent of ionization is much less. The net charge (dotted line) and zeta potentials are the same in both cases, but adsorption interactions on a mineral surface would probably be quite different for these two cases. In case (a) there are many charged sites. Details of their short range interactions with a surface would depend on their distribution, but there are many sites that could attract or repel a charged surface. The surface illustrated in (b) is nearly uncharged over a broad range of pH. These two hypothetical interfaces might behave similarly at high or low pH, but be quite dissimilar near their point of zero charge.

Isoelectric point: The pH at which the numbers of negative and positive charges are equal is the isoelectric point (IEP). This is different from a point of zero charge in that the interface may be highly charged, but the net charge is zero. The important factors in determining IEP are the relative numbers of acidic and basic sites, the average pK_a and the difference between $pK_a(\text{acid})$ and $pK_a(\text{base})$, as shown in Fig. 3-11. If $pK_a(\text{base}) = pK_a(\text{acid})$, the relationship between IEP and $N_a(\text{acid})/N_a(\text{base})$ is linear. As the difference between the

two pK_a values increases, the IEP becomes increasingly sensitive to the ratio $N_a(\text{acid})/N_a(\text{base})$.

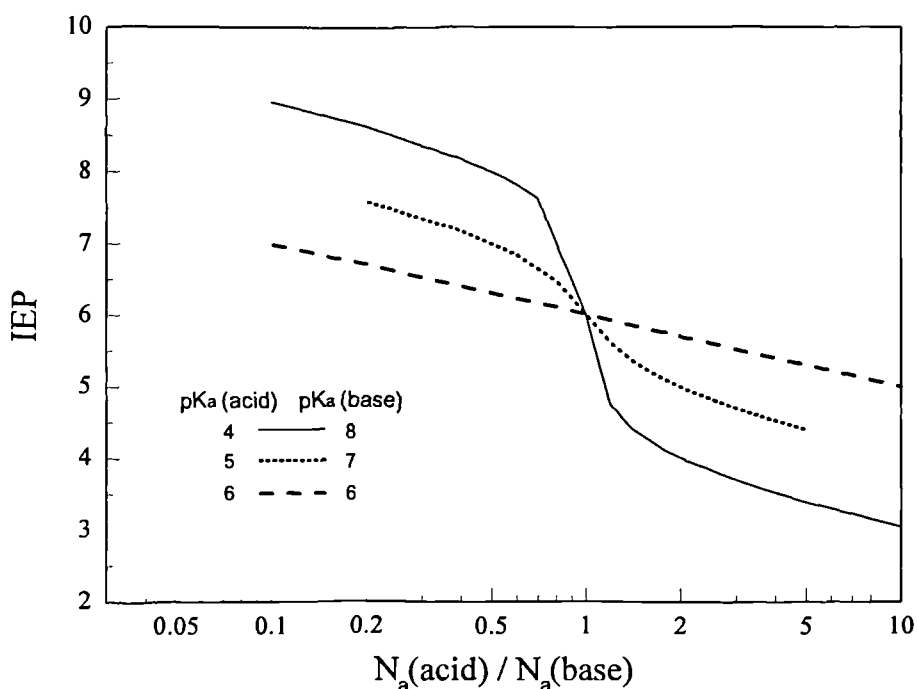


Figure 3-11. The isoelectric point of a zwitterionic surface depends strongly on the ratio of the numbers of acidic sites and basic sites, and their respective pK_a values.

Crude oil/brine interfaces—positive, negative, and net charge: Zeta potential measurements for Moutray crude oil have been shown to be consistent with an interface with both acidic and basic functional groups and ISG parameters as shown in Fig. 3-12 (Buckley *et al.*, 1989). pK values are separated by 2 pH units with $pK_a(\text{acid}) < pK_a(\text{base})$, with about four acidic sites for each basic site. IEP is near pH 4 and there is positive as well as negative charge up to pH 8 or higher ($I = 0.01 M$).

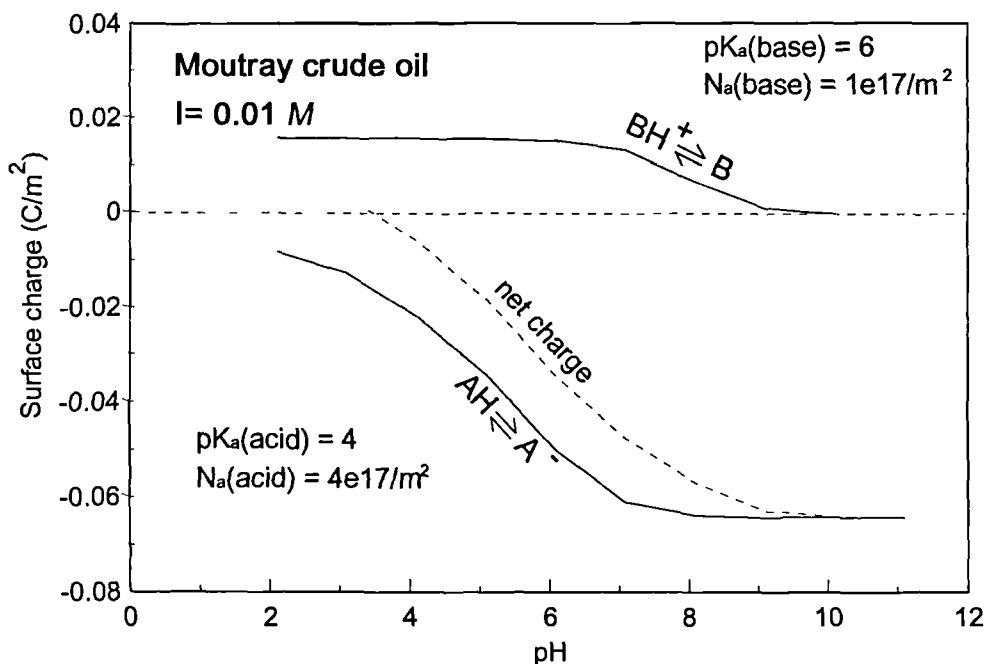


Figure 3-12. Surface charge of zwitterionic Moutray crude oil emulsions. (calculated from data in Buckley *et al.*, 1989)

Crude oil/brine interfaces—IFT: For interfaces with either acidic or basic functionality, IFT varied with interfacial charge, either positive or negative. More highly charged interfaces have lower IFT between oil and brine. How does this observation apply to interfaces with both positive and negative charge (crude oil/brine interfaces for instance)?

In Fig. 3-13 ionization of the basic functional groups of the Moutray crude oil interface is shown. The 0.01M NaCl case is repeated from Fig. 3-12 along with similar calculations for lower and higher ionic strength solutions. IFT measurements between Moutray and 0.01 M NaCl brines with varying pH can be seen to follow transition of the basic sites from positively charged to neutral. This occurs well above the pH at which the interface gains a net negative charge (about pH 4) and even above the full ionization of acidic groups (about pH 7). What appears to be important in controlling IFT is the transition from an interface with both positive and negative sites (zwitterionic) to one with only negatively charged sites.

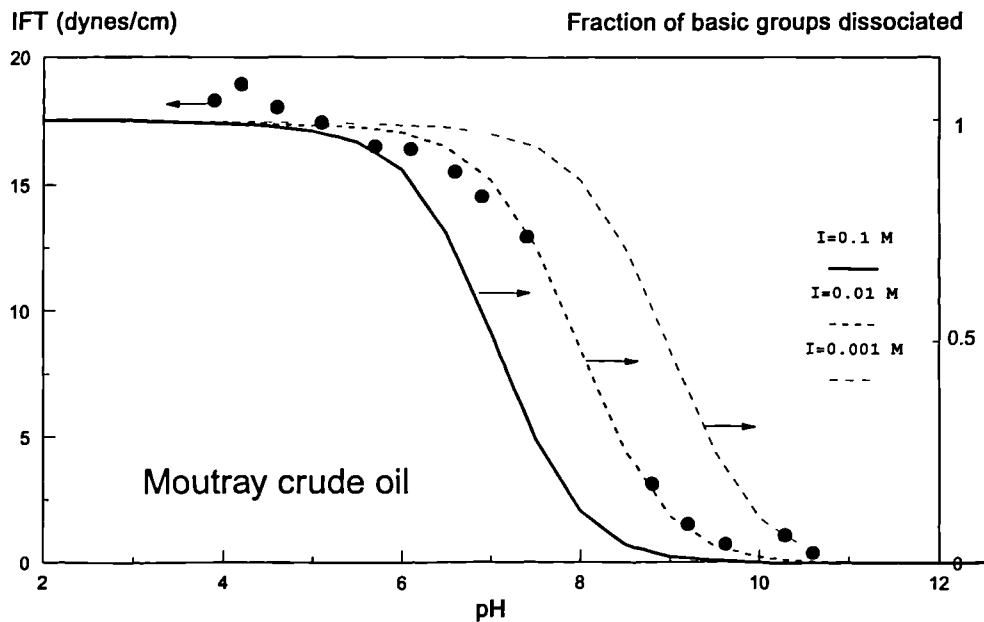


Figure 3-13. Positively charged ionizable sites for Moutray crude oil with brines of varying pH and ionic strength. The best match to the IFT data for measurements against 0.01 M NaCl brines is with the calculated 0.01 M curve.

A second example, ST-86 crude oil is shown in Fig. 3-14. Interfacial tension appears to be a fairly sensitive indicator of the transition from zwitterionic conditions to a surface that has exclusively positive or negative charges, although more evidence is needed to confirm that this is a general property of crude oil interfaces.

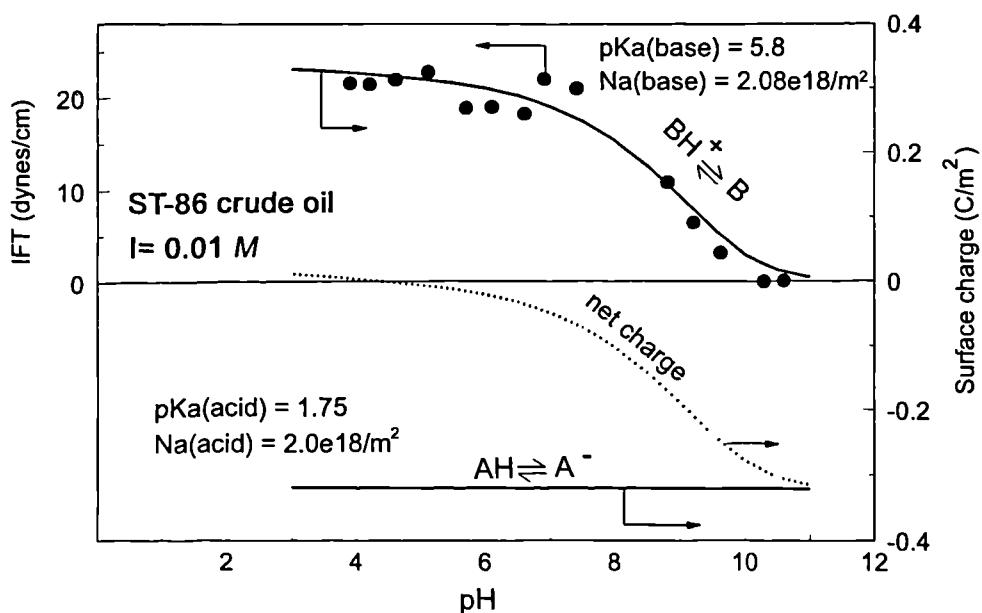


Figure 3-14. Comparison of zwitterionic surface charges and IFT for ST-86 crude oil. (calculations based on data from Buckley *et al.*, 1989)

Fig. 3-15 shows zeta potential measurements for A-93 crude oil that establish an IEP of about 3. Interpretation of these zeta potential measurements by the ISG method has so far been unsuccessful.

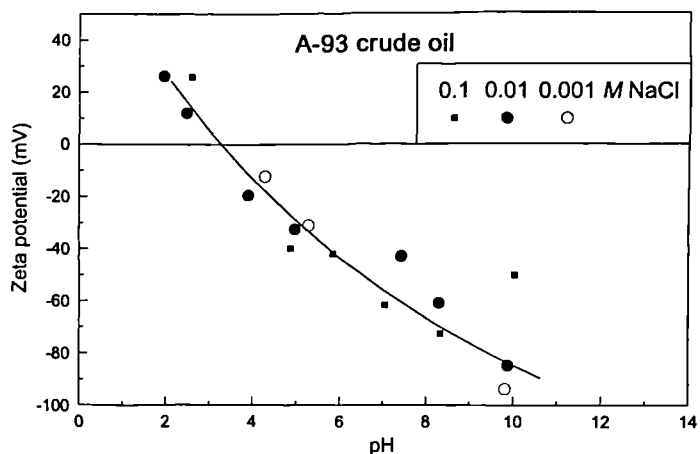


Figure 3-15. Zeta potential measurements for A-93 crude oil emulsions.

Oil/Brine/Solid Interactions

The third important ingredient involved in COBR interactions is the rock. The pore surfaces of rocks are complex, both chemically and physically. Many minerals may be present at the surfaces of pores. Some of these may dominate the surfaces while constituting only a small fraction of the bulk mineralogy of the rock. The details of interaction between crude oil components and each mineral will differ. Depending on the specific minerals involved, some portions of the pore surface may be more likely to adsorb crude oil components because of the distribution of more reactive minerals. Consideration of different mineral types is largely beyond the scope of this study, although it is certainly an important area for future work.

Mineral surfaces, like the oil/brine interfaces, are charged in aqueous environments. The approach of two differently charged interfaces can have one of several different results. A key issue is the disjoining pressure (Π) in the water film as the

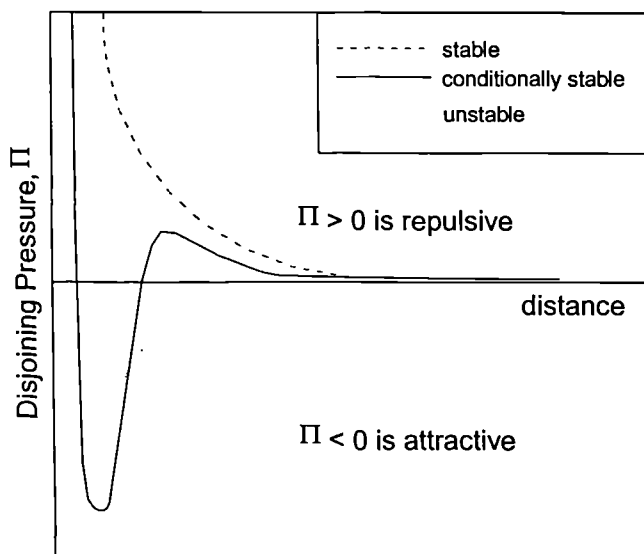


Figure 3-16. Illustration of three general shapes of disjoining pressure vs separation distance relationships.

two interfaces approach one another (illustrated in Fig. 3-16). The concept of disjoining pressure was first suggested by Derjaguin (1987). Introductions are given in many surface and colloid chemistry texts (e.g., Israelachvili, 1991). Π arises as the result of van der Waals, electrostatic, and other forces effective over separation distances on the order of 100 nm or less. These contributing forces are summed to give the net values of Π as shown in Fig. 3-16. Hirasaki (1991) extended these concepts specifically to wetting of oil/brine/solid systems and calculated contact angles as a function of film thickness.

If the value of Π is positive (by convention positive values are repulsive) for all values of separation distance, the water film is stable and water-wet conditions can be maintained. The classic example of strongly water-wet conditions maintained over geologic time is the Athabasca tar sands deposit (Takamura and Chow, 1983 and 1985).

At the other end of the spectrum are unstable disjoining pressure curves where Π is always negative (attractive). Crude oil/mineral interactions may often fall between these two extremes where the approaching interfaces may experience either attraction or repulsion, depending on capillary pressure, temperature, and other environmental factors. Adsorption may be slow and it may even be reversible.

The physical complexities or roughness of rock surfaces combine with water as the initial pore-occupying phase to protect some surfaces from contact with oil. Bulk water resides in corners and in the smallest pores. The thin-film considerations of disjoining pressure and water film stability do not apply where bulk water remains and strongly water-wet surfaces can be preserved. Conversely, there are asperities where the water film thins to a greater extent because of the shape of pore surfaces. Asperities are more vulnerable to water film rupture than are flat surfaces under otherwise similar conditions. This is a consequence of the augmented Young-Laplace equation:

$$P_c = \gamma (1/r_1 + 1/r_2) + \Pi$$

where P_c is the capillary pressure or difference between nonwetting phase and wetting phase pressures, γ is the interfacial tension, and r_1 and r_2 are radii of curvature. A good discussion of the transition between a thin film at a surface and a meniscus between two bulk liquids is given by Hirasaki (1991). Some rock surfaces, therefore, will be more likely to remain water-wet and others more subject to wetting alteration by adsorption because of the roughness of the surface.

Experimental observations—background

Reisberg and Doscher (1956) investigated pH-dependent interfacial properties of Ventura crude oil. In addition to the variation of IFT with pH alluded to previously, they observed cleaning of oil from glass slides and were surprised to note that oil could, depending on pH, adhere more tenaciously to wet glass than to dry.

A variety of phenomenological tests that demonstrate COBR interactions have been reported. Brown and Neustadter (1980) reported both contact angles and engulfment tests in support of pH and salinity-dependent COBR wetting with Forties crude oil. Dubey and Doe (1993) used visual observations of oil and brine in contact with sand grains in what they called bottle tests to determine the brine conditions for which about half the oil was released and half remained adhering to the sand. Takamura and Chow (1983) videotaped the release of bitumen from tar sands to show the effects of brines with and without addition of divalent ions.

Contact angle measurements have been used by many investigators to assess COBR wetting (c.f. Anderson, 1986b and references cited therein). Contact angle measurements were adapted by Leach *et al.* (1962) to the observation of hysteresis in crude oil, brine, solid systems. A drop of crude oil was trapped between two crystal surface as shown in Fig 3-17a. Movement of the crystals in opposite directions allowed measurements of both advancing and receding contact angles. After each movement of the crystals, some time had to elapse before stable interface positions were achieved. Treiber *et al.* (1972) used this technique to test the wetting of more than 50 reservoirs. Water receding contact angles are generally low and were judged not to represent reservoir wetting. Advancing angles can be quite high and vary with aging time. A disadvantage of this technique, beyond the long equilibration times required, is the pinning of the three-phase line of contact that can prevent the advance of the interface.

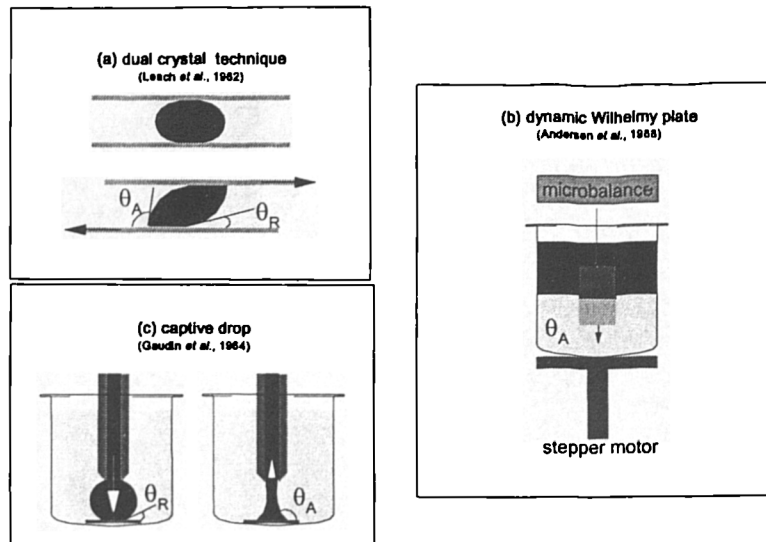


Figure 3-17. Contact angle measurement techniques. Hysteresis between water receding and water advancing conditions is commonly observed for crude oils.

Contact angles can also be measured without optical observations using a technique introduced by Wilhelmy (1863). The force, F , acting on a suspended plate, passing through the interface between immiscible fluids is given by

$$F = F_i + F_b$$

where F_i and F_b are the interfacial and buoyancy forces, respectively. The interfacial force is related to the plate perimeter, p , the interfacial tension, γ , and the contact angle, θ , by

$$F_i = p \gamma \cos\theta$$

If the plate surface is smooth and homogeneous, the contact angle along the perimeter is unique. The effects of hysteresis are shown using a dynamic technique (Andersen *et al.*, 1988), illustrated in Fig. 3-17b. As the plate moves upwards through the oil/brine interface, water receding conditions apply; when the motion of the plate is reversed, water advances. Pinning of the interface occurs, but can sometimes be overcome, if the plate is sufficiently long (Mennella *et al.*, 1995).

Another approach to measuring advancing and receding angles is the captive drop technique (Gaudin, 1964). As illustrated in Fig. 3-17c, an oil drop is trapped between a

surface and the tip of a burette on which the oil drop is formed. Advancing and receding conditions are investigated by increasing and decreasing the size of the drop. This technique, too, can suffer limitations from pinning of the three-phase contact line, but as adapted here, it has allowed extensive exploration of the interactions among crude oils, brine, and solid surfaces. These adaptations are of two kinds:

- a semiquantitative mapping of the brine conditions under which rapid **adhesion** of oil drops on the solid occurs, and
- alteration of surface wetting by **adsorption** of crude oil components.

Using these two techniques and comparing the information they provide can help to define the interfacial interactions of particular crude oils.

Adhesion

Captive drops of crude oil display widely divergent contact angles, depending on whether or not the contact line is pinned. In constructing adhesion maps, rather than measure these highly variable contact angles, conditions are identified for which the oil drop rapidly adheres to the solid surface. The technique was introduced by Buckley *et al.* (1989) and the results explained in terms of the stability of a layer of water between the solid and oil phases. If the aqueous phase is a solution of monovalent ions of relatively low ionic strength (e.g. less than 1 M NaCl), interpretation of the results in terms of DLVO (van der Waals and electrical double layer) forces is satisfactory, although not exact; adhesion is often observed with higher pH solutions than is predicted by the DLVO calculations. ISG models can be used to estimate the interfacial charge for both oil/brine and solid/brine interfaces and the stability of the intervening water film predicted as a function of brine composition (pH and ionic strength). Simplifying assumptions regarding the surface shapes (two plates, plate and sphere, etc.), Hamaker constants to describe material properties, and constant charge or constant potential assumptions about the behavior of the charged interfaces at very small separation distances are all required to make these calculations. Limitations to the theory include:

- interactions with high salinities brines,
- non-DLVO forces, and
- specific interactions involving ions of valence higher than ± 1 .

For most cases of realistic interest, therefore, experimental observations are essential.

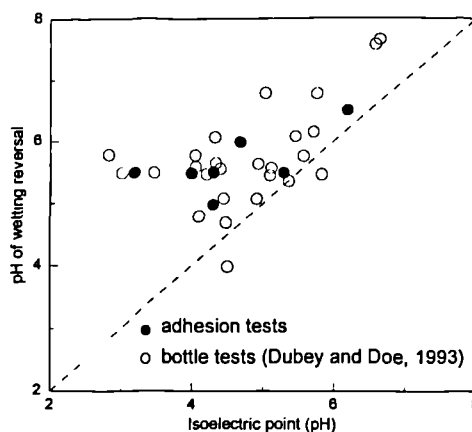


Figure 3-18. Transition from water-wet to oil-wet, as judged by either adhesion or bottle tests, generally occurs well above the isoelectric point for zwitterionic crude oil interfaces.

Adhesion and IEP: Fig. 3-18 compares the isoelectric point of two sets of crude oils with the pH at which a wetting transition occurs on negatively charged silica surfaces (i.e. the pH above which more water-wet conditions are maintained and below which wetting is altered to more oil-wet). Each data point is a different crude oil. Isoelectric points were determined by electrophoresis. Wetting reversal was judged either by bottle tests using silica sand (Dubey and Doe, 1993) or by adhesion on glass microscope slides (as described in Appendix B). Some of the scatter in the comparisons is no doubt due to imprecision of these semiquantitative methods of assessing wetting reversal. Unique surface chemistry of each crude oil is another factor that can be expected to contribute scatter. Nevertheless, both adhesion and bottle tests demonstrate that wettability alteration, as measured by these two simple tests, can and often does occur well above the IEP.

Stability of water films: The adhesion map separates the brine composition space into two regions: adhesion and nonadhesion. Referring to the disjoining pressure diagram (Fig. 3-16), there should be at least three regions where water films are unstable, stable, and conditionally stable. Where there is a stable water film, there should not be any adhesion of oil. If the water film is unstable and breaks, adhesion can occur. Whether there is adhesion in the conditionally stable case must depend on the shape of the disjoining pressure curve and on external variables, especially capillary pressure. One possible explanation for the observations of adhesion well above the IEP (Fig. 3-18) is that adhesion is occurring in the conditionally stable region. If the positive maximum is low with respect to capillary

pressure, it presents no real barrier to adhesion. In that case, whether adhesion occurs would depend on the depth of the attractive minimum.

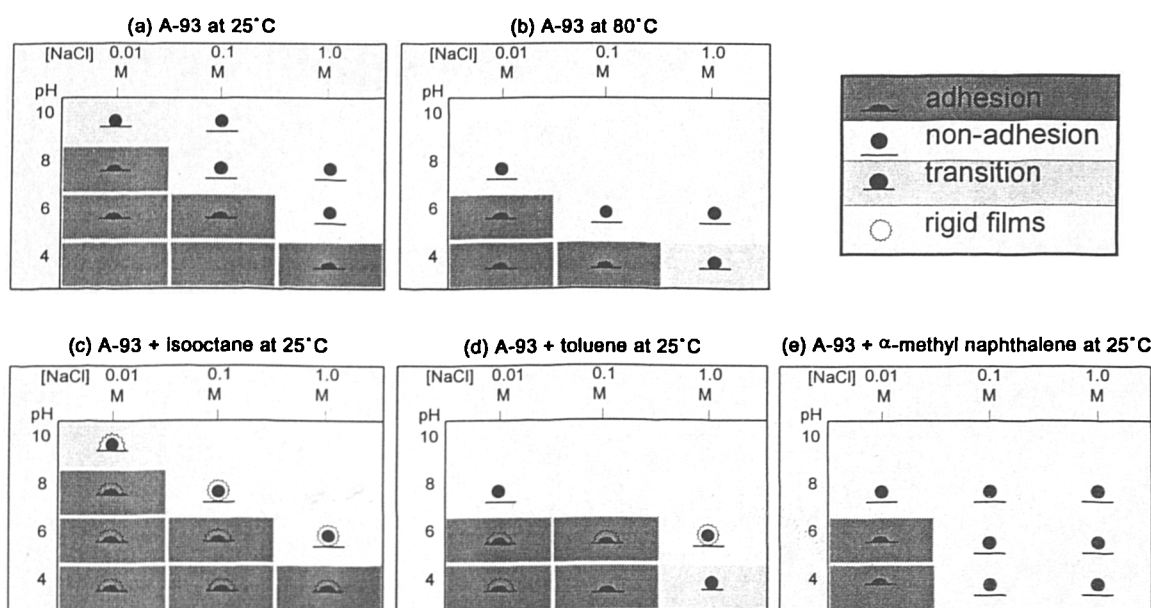


Figure 3-19. Adhesion maps for A-93 crude oil and mixtures of oil with precipitants and solvents: (a) 100% crude oil at 25°C, (b) 100% crude oil at 80°C, (c) 40% crude oil + 60% isooctane at 25°C, (d) 40% crude oil + 60% toluene at 25°C, and (e) 40% crude oil + 60% α -methyl naphthalene at 25°C. Adhesive region decreases with increasing temperature and addition of solvents.

Effect of temperature on adhesion: The results of very brief (approximately 2 minutes) exposure of glass to a captive drop of A-93 crude oil are shown in the adhesion maps in Fig. 3-19. Measurements were made at both 25°C (Fig. 3-19a) and 80°C (Fig. 3-19b) spanning a range of brine compositions from pH 4 to pH 10 and sodium ion concentrations from 0.01 M to 1.0 M. Figs. 3-19c-e show additional adhesion maps for A-93 crude oil mixed with precipitant (isooctane) or solvents (toluene and α -methyl naphthalene). Referring first to Figs. 3-19a and b, three conditions can be identified: those where adhesion does not occur at either temperature (generally with high pH brines), conditions where adhesion is observed at both temperatures (low pH and low ionic strength), and finally there are conditions where adhesion is observed at room temperature but not at 80°C.

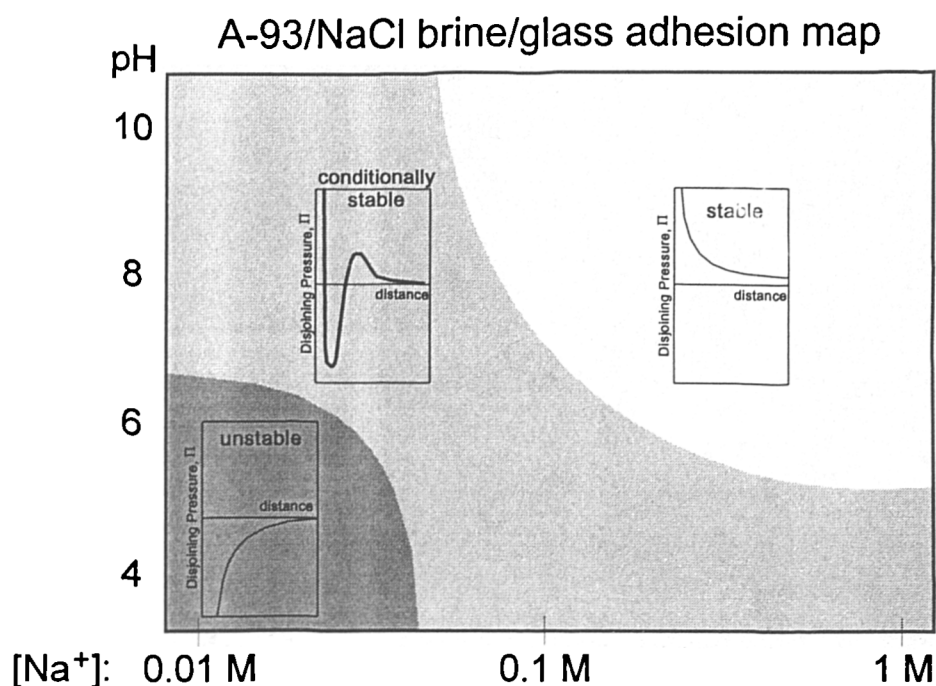


Figure 3-20. Temperature-dependent and solvent-dependent adhesion results can be divided into three regions where: (1) nonadhesion is always observed, (2) adhesion is always observed, and (3) adhesion or nonadhesion can occur, depending on temperature or solvent properties. These correspond to water films that are (1) stable, (2) unstable, and (3) conditionally stable, as shown.

The A-93/NaCl brine/glass adhesion map, divided into these three regions, is shown in Fig. 3-20. The three regions are tentatively identified with unstable, stable, and conditionally stable disjoining pressure isotherms, respectively.

Increasing temperature has a significant effect on the size of asphaltene aggregates in the oil (see Figs. 2-4c and d). Changing aggregate size might affect the extent of interaction among the discrete positively and negatively charged species, as illustrated in Fig. 3-21. Charged sites can interact more or less independently with the surface depending on the size of aggregates of which they are part. Attraction between sites with positive charge and the negatively charged silica surface is illustrated in Fig. 3-21a for large aggregates with relatively low surface charge density. As aggregate size decreases, surface charge density increases and interactions between neighboring aggregates become stronger. Independent interactions between aggregate and solid are less favored; attractive and repulsive forces balance one another (Fig. 3-21b).

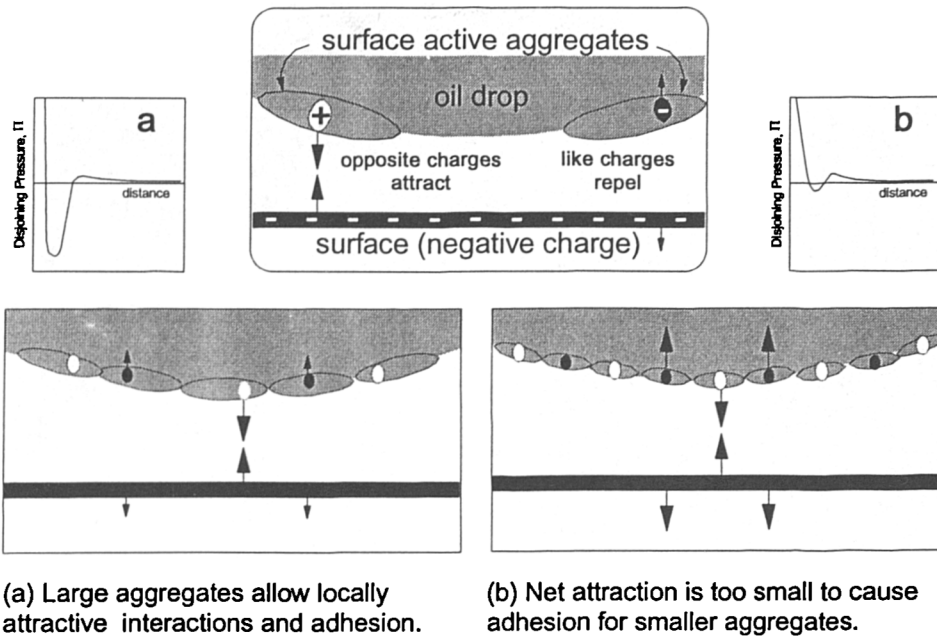


Figure 3-21. Disjoining pressure can depend on the size of asphaltene aggregates and the extent to which independent action between discrete charged sites is allowed.

This picture is consistent with previously reported results (Jadhunandan and Morrow, 1995) showing a greater degree of wetting alteration in cores using Moutray crude oil than ST-86 (Fig. 3-22) since surface charge density estimates are much higher for ST-86 than for Moutray.

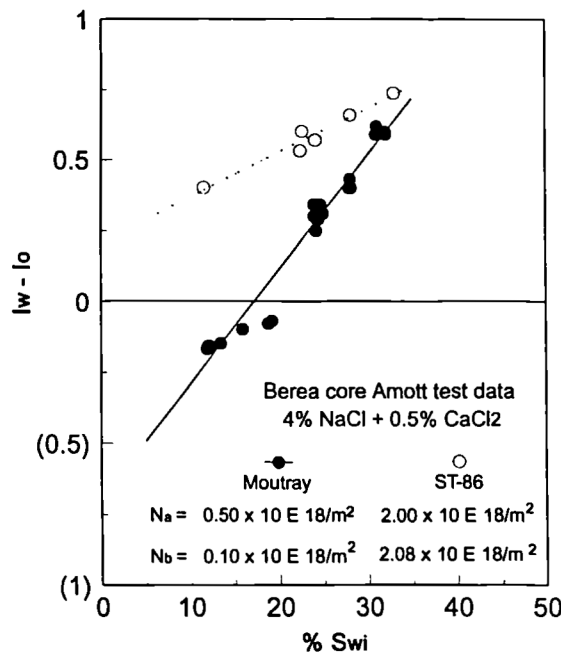


Figure 3-22. Charge densities (from Buckley *et al.*, 1989) of Moutray and ST-86 crude oils and Amott-Harvey indices for tests of these crude oils in Berea sandstone (from Jadhunandan and Morrow, 1995) show greater alteration of wetting under comparable conditions of initial water saturation for Moutray which has the lower surface charge density.

Effect of changes in oil composition on adhesion: Support for the influence of aggregate size on COBR interactions comes from some additional adhesion experiments using solvents and precipitants to alter asphaltene aggregation. Samples of A-93 crude oil were mixed with isooctane (Fig. 3-19c), toluene (Fig. 3-19d), and α -methyl naphthalene (Fig. 3-19e). In each case, the volume of crude oil was 2/3 that of the added hydrocarbon (volume fraction of crude oil in the mixture equals 0.4). Refractive indices of the mixtures of isooctane and toluene with crude oil are included in Fig. 3-23. Although the isooctane mixture was close to the onset of precipitation, no asphaltene particles could be observed by microscopic inspection. For the isooctane mixture (Fig. 3-19c), the adhesive region is the same as that for the crude oil (Fig. 3-19a). There is one major difference: rigid films are formed in nearly all tests, including those with stable water films. When the oil was mixed with toluene, the adhesive region was reduced, similar to that for the crude oil at 80°C.

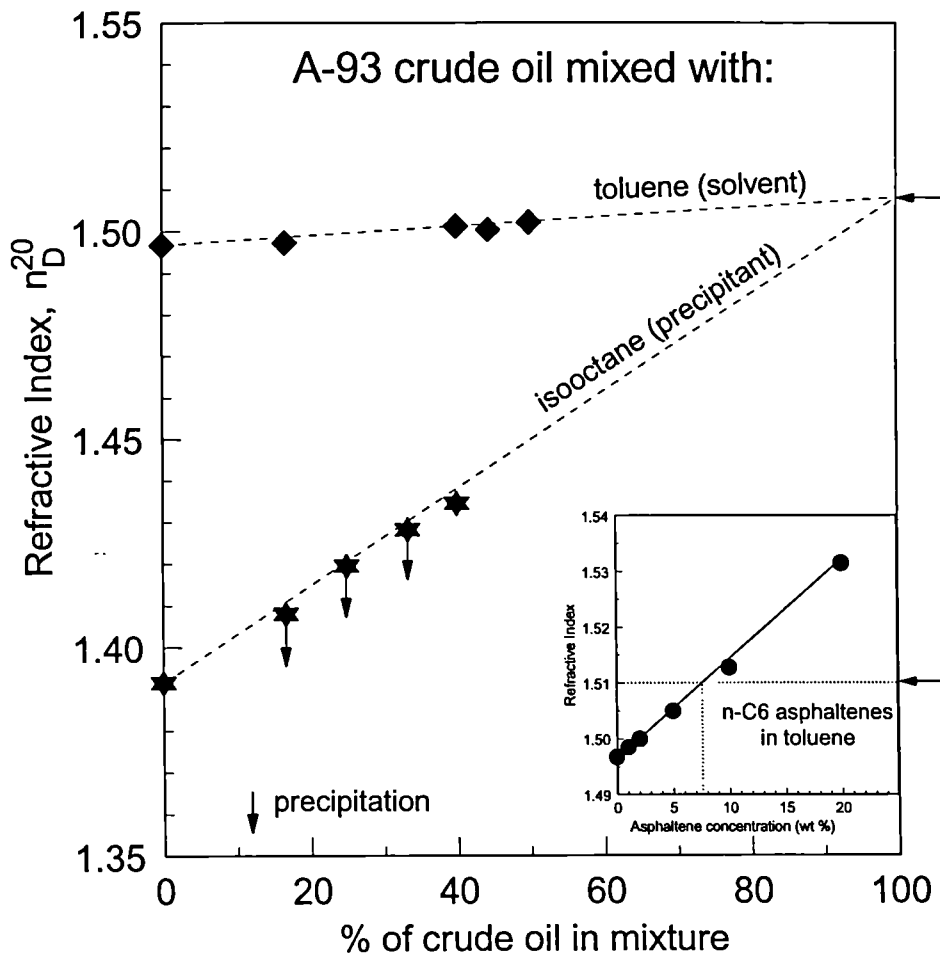


Figure 3-23. Refractive indices for mixtures of A-93 crude oil with toluene (solvent) and isooctane (precipitant). Extrapolation to 100% crude oil gives an estimate for the refractive index of the oil of 1.51. Inset shows refractive indices measured for solutions of n-hexane asphaltenes prepared from A-93 crude oil, dissolved in toluene.

Addition of isooctane makes the oil a poorer solvent and increases aggregate size. Addition of toluene appears to have the opposite effect. Using α -methyl naphthalene (Fig. 3-19c), with a refractive index higher than the oil, adhesion remained only for the lowest ionic strength, pH 4 and pH 6 solutions and no rigid films were observed.

The effects of temperature and solvent on attractive forces proposed here are roughly analogous to the attractive intersegment and bridging forces observed for polymer solutions. For polymers, these attractive forces are most significant under poor solvent conditions (below the theta temperature) (Israelachvili, 1991). These observations may lend support to the arguments of Cimino *et al.* (1996) that asphaltenes are best described as lyophilic colloids, with many similarities to polymers.

Adhesion in mixed brines: Previous studies have demonstrated that adhesion results with divalent calcium ions added to the brine are quite unpredictable and crude oil-specific (Buckley and Morrow, 1991). When A-93 crude oil was tested with its synthetic reservoir brine (containing both Ca^{2+} and Mg^{2+}), the results were nonadhesive. This was true whether the tests were conducted at 25 or 80°C. With this brine, however, changes in wetting of glass surfaces can be observed in other tests, as reported by Liu and Buckley (1995). Contact times of at least 4 hours are required before pinning begins to indicate that wetting changes are occurring at 80°C, much longer than the few minutes typically allowed for adhesion observations.

Adsorption

Equilibration of a crude oil drop for long periods of time can result in contact angles that are dominated by pinning of the three-phase contact line. To avoid this problem so that COBR interactions can be monitored over the longer periods of aging time typical of laboratory experiments in cores, a technique to test for adsorption of crude oil components was developed (Buckley and Morrow, 1991), using a sequential approach to surface treatment. Surfaces were first aged in selected brine solutions, then in crude oil, after which the oil was removed by rinsing with solvents. Changes in wetting of the solid surface were assessed by measurements of contact angles of pure fluids, usually water and decane. This technique, the details of which are included in Appendix B, has been tested with the standard set of NaCl brines, synthetic reservoir brines, and with no brine (i.e. surfaces are dry when first exposed to crude oil, as discussed in Chapter 2). Four crude oils (A-90, A-93, Schuricht,

and Sulimar Queen; refer to Appendix A for fluid properties) have now been tested dry and with the complete set of NaCl brines. Aging temperatures of 25 and 80°C and aging times from hours to weeks have been compared. The results, reviewed here, have been reported in detail elsewhere (Liu, 1993; Liu and Buckley, 1994; Liu and Buckley, 1995; Buckley *et al.*, 1996; Wu, 1996). In addition to the compositions of fluid and solid phases, experimental variables include aging times, aging temperatures, and the solvents used to remove bulk crude oil.

Adsorption of water soluble oil components: To some extent, adsorption of crude oil components must occur through bulk water. All of the rock surface is equally available for adsorption and wetting alteration by this mechanism. If this were the principal mechanism of wetting alteration, the extent could be controlled mainly by differences in mineralogy. The wetting conditions that result would be expected to be either uniform, if there is little differentiation in the effect of oil compounds on *different surfaces*, or *fractionally (dalmation)* mixed-wet, if distinct differences in adsorption onto different mineral surfaces occur.

To test the extent to which wetting is changed by crude oil components with significant water solubility, A-93 crude oil was equilibrated with several different brines at 80°C overnight. Oil and water were separated and glass slides were aged in the separated water phases at 80°C. Contact angles, measured with the slides submerged in these respective water phases with a drop of decane, are given in Table 3-2.

Table 3-2. Adsorption of water-soluble components of A-93 crude oil.				
brine	5 hours aging		8 days aging	
	θ_A	θ_R	θ_A	θ_R
pH 4, I=0.1 M	18	17	31	26
pH 10, I= 0.1 M	22	29	30	29
A-93 synthetic reservoir brine	23	21	33	28

The results in Table 3-2 show that water-wet conditions are maintained on surfaces exposed to water-soluble crude oil components. Given geological time, the effects of adsorption through bulk water may become important, but they are unlikely to contribute to the dramatic changes in contact angles observed on laboratory time scales. Thus pore morphology and initial distribution of fluids can control the pattern of mixed wetting that develops in laboratory core samples aged in crude oil. In subsequent tests, therefore, samples

were initially equilibrated in various brines, but the water was allowed to drain off before the slides were submerged directly into oil.

Removal of bulk crude oil after aging: In order to assess the altered wetting on surfaces aged in crude oil, the bulk oil must be removed. The extent to which adsorbed material is retained during the washing step is critical to the validity of these tests. Table 3-3 shows the results of various washing techniques on surfaces treated with A-93 crude oil. If an adsorbed layer has been established during the aging process, extensive washing with strong solvents could remove part or all of it. At the other extreme, decane (or other low molecular weight paraffins) can cause asphaltene aggregation during the washing step, leaving the surface strongly oil-wet. Fig. 3-23 shows the change in refractive index as isooctane and toluene are mixed with A-93 crude oil. Isooctane reduces refractive index and eventually causes precipitation, whereas toluene changes refractive index of the mixture only slightly. Removal of bulk oil without greatly altering oil solvency is best approximated by washing with toluene, as shown in Table 3-3. Cyclohexane is another alternative, although with some oils, cyclohexane can be a precipitant.

Table 3-3. Comparison of the effect of washing techniques on contact angle measurements.				
pretreated with synthetic reservoir brine, aged in oil at 80°C				
washing agent	solvent/precipitant	rinse/soak	θ_A	θ_R
decane	precipitant	rinse	180	> 150
cyclohexane	weak solvent	soak	156 ± 6	30 ± 2
toluene	solvent	rinse	156 ± 6	30 ± 3
toluene	solvent	soak	125 ± 34	21 ± 6

Effect of temperature on adsorption: What remains after washing with toluene on surfaces aged for periods ranging from a few hours to a month or more, tells a somewhat different story from the two minute adhesion experiments discussed previously. Fig. 3-24 shows examples of the advancing angles measured with water and decane after aging either at room temperature or at 80°C for combinations of two different oil samples (A-90 and A-93) and two brine compositions:

- 0.01 M NaCl brine with pH 4, and

- A-93 synthetic reservoir brine.

With the first of these brines, adhesion is immediate at both 25 and 80°C for both oils. In the case with synthetic reservoir brine, on the other hand, adhesion of oil is not observed in the 2 minute test. The results in Fig. 3-24 show an additional dependence on temperature that was not evident in the adhesion test in either case.

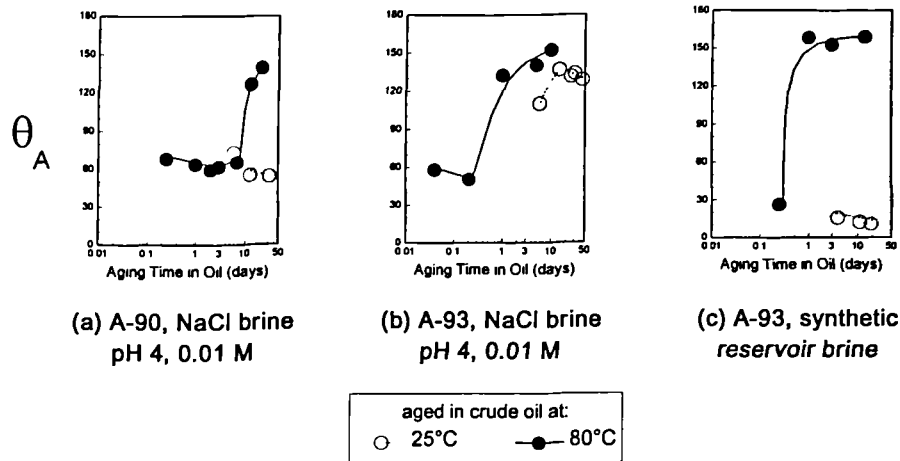


Figure 3-24. Induction times (indicated for 80°C data by the unshaded portion of each plot) can vary with crude oil, brine, and aging temperature.

All three oil/brine combinations in Fig. 3-24 demonstrate instances of two stage adsorption (Liu and Buckley, 1995). There is an immediate jump from strongly water-wet conditions ($\theta_A = 0$ degrees) to weakly water-wet ($30 \leq \theta_A \leq 70$ degrees), followed in some cases by a second increase to much higher, more oil-wet, contact angles. The second increase (for 80° aging) is indicated in each of these figures by the shaded area. The induction time before the second stage of adsorption ranges from a few hours (Fig. 3-24c) to more than a week (Fig. 3-24a). In one of the three cases (Fig. 3-24b), high advancing angles are measured on surfaces aged in oil at both 25 and at 80°C, although the induction time may be longer at 25 than at 80°C. Although much remains to be explained about the kinetics of these complex processes, the strong temperature dependence suggests that adsorption, after the water film has broken, is a relatively slow, kinetically controlled, process. With geologic time available for adsorption, however, reservoir conditions can be expected to approach the high temperature results, whenever the water film is unstable.

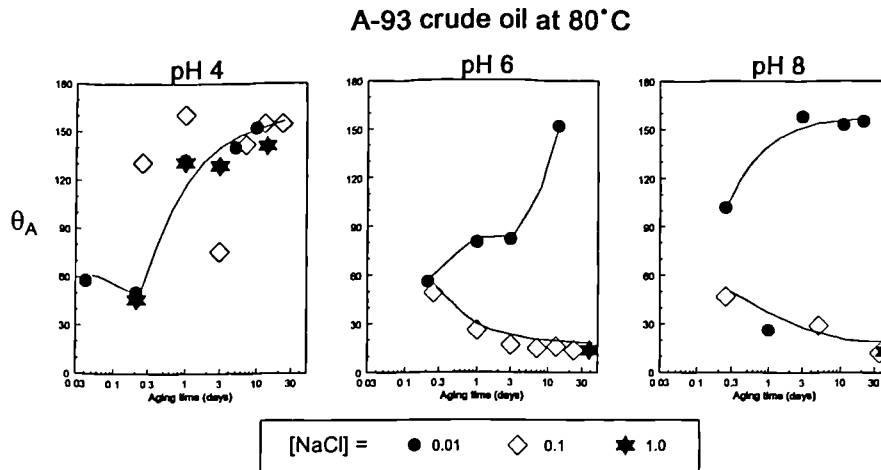


Figure 3-25. Both brine pH and ionic composition are important in determining the contact angle on glass surfaces aged in crude oil.

Adsorption—NaCl brines of varying concentration and pH: From the adhesion test, we have an outline of the NaCl brine conditions for water film stability (Fig. 3-20). Adsorption over a range of pH and NaCl concentrations is shown for aging in A-93 crude oil at 80°C in Fig. 3-25a-c. In Fig. 3-26, these same data are replotted. In this case, the symbols distinguish different brines on the basis of adhesion results. For less than a week of aging, there is considerable scatter in the results. For aging times longer than one week, however, two clear trends emerge. One set of slides has high advancing angles, on the order of 155 degrees; for the other set, advancing angles are low, about 15 degrees. All of the conditions judged to have unstable water films on the basis of adhesion tests are in the high advancing angle group, whereas all of the stable water film brines are in the low group. Conditionally stable brines are represented in both groups.

A-93 crude oil at 80°C

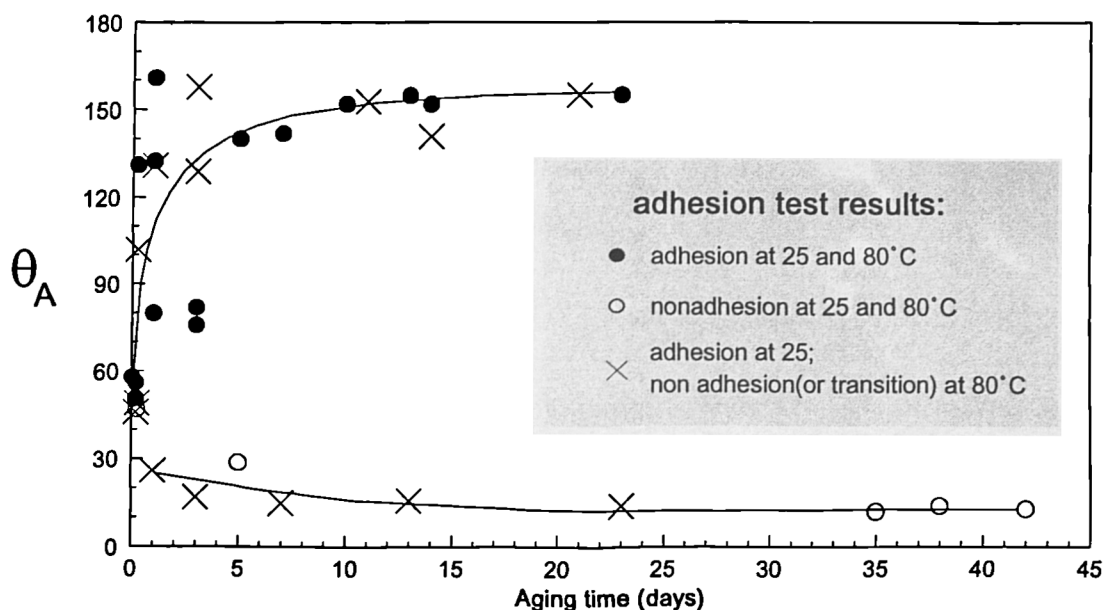


Figure 3-26. High contact angles develop for all the oil/brine/solid ensembles for which adhesion occurs at 80°C. Nonadhesion at 25°C corresponds to low advancing angles. For the cases where adhesion occurred at 25°C, but not at 80°C, adsorption results in either high or low angles, with a clear distinction between these two cases.

These results are consistent with the zwitterionic interface suggested in Fig. 3-21. With respect to a negatively charged silica surface, stable conditions are those where the oil/brine interface has few positively charged sites (not just a net negative charge), whereas unstable conditions are those with few negatively charged species. Interactions can occur in the middle ground where both positive and negative sites exist, as evidenced by adhesion at low temperature, but they may never be strong enough to withstand even the gentle toluene rinse that is part of the adsorption test procedure.

Adsorption—mixed brines: While a detailed study of the effects of additional salts either in place of or added to NaCl has yet to be reported, some results with mixed brines are available. Fig. 3-24c is a typical example. The brine is a mixture of sodium, potassium, magnesium and calcium chlorides made up to approximate the reservoir brine composition for Prudhoe Bay. Strong adsorption is observed at 80°C after only one day of aging. The details of interfacial chemistry are likely to be complicated since the divalent cations can bind at both the silica and oil interfaces. In addition they can bridge between two negative sites,

one on the solid and the other on the oil. Competition between all of these interactions will influence the outcome of aging in the presence of divalent and multivalent ions.

Adsorption—effect of changes in oil composition: Only a limited number of measurements have been made in which the oil composition has been systematically varied. These data, shown in Table 3-4, present an interesting trend that suggests an avenue for future research. Addition of solvents to the oil reduced the value of advancing contact angle on treated surfaces to. These measurements were made on surfaces pretreated with the synthetic reservoir brine, aged in mixtures of 40% crude oil and 60% added solvent or precipitant. Additional measurements for varying periods of time are needed to determine whether these are maximum values or if the addition of solvents slows the adsorption process. Likewise, it is not possible to say whether the reduced contact angles result from submonolayer coverage or uniform coverage with a thinner hydrocarbon layer.

Table 3-4. Effect of precipitants and solvents on adsorption from A-93.				
pretreated with synthetic reservoir brine, aged in oil for 2 weeks				
at 80°C, captive drop measurements				
A-93 crude oil (%)	Mixed with	(%)	θ_A	θ_R
100	n/a		159 ± 10	41 ± 8
40	isooctane(precipitant)	60	161 ± 12	96 ± 35
			159 ± 10	82 ± 27
40	toluene (solvent)	60	90 ± 5	25 ± 2
			89 ± 8	23 ± 5
40	α -methyl naphthalene	60	71 ± 12	18 ± 4
			72 ± 10	18 ± 3

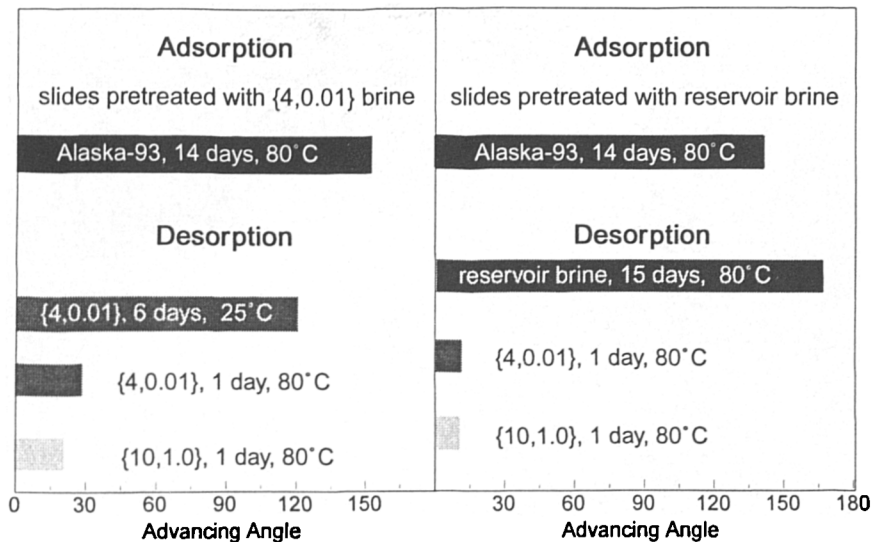


Figure 3-27. Desorption of crude oil components can occur, depending on temperature and on the brine compositions both before and after aging in oil.

Desorption: Liu (1993) observed that after adsorption of crude oil components raised advancing angles on glass surfaces to high values, further changes could be induced by submerging the surface in brine. Fig. 3-27 summarizes observations of desorption with varying initial conditions, desorbing brines and desorbing temperatures. Desorption was slower for samples initially soaked in the synthetic reservoir brine, faster at higher temperature, and faster if the desorbing brine is different than the adsorbing brine. Changes in reservoir wetting during a waterflood may reflect this kind of desorption phenomenon.

Atomic forces microscopy

Samples for atomic forces microscopy (AFM) studies were prepared by aging in crude oil at 80°C for three weeks. Bulk crude oil was removed by rinsing with solvent or precipitant, after which the samples were dried. AFM measurements were made at the Savannah River Ecology Laboratory using a tapping technique that minimizes contact between graphite tips and the sample surface (Sullivan *et al.*, 1995). The AFM interprets changes in the force between tip and surface as differences in height on the surface.

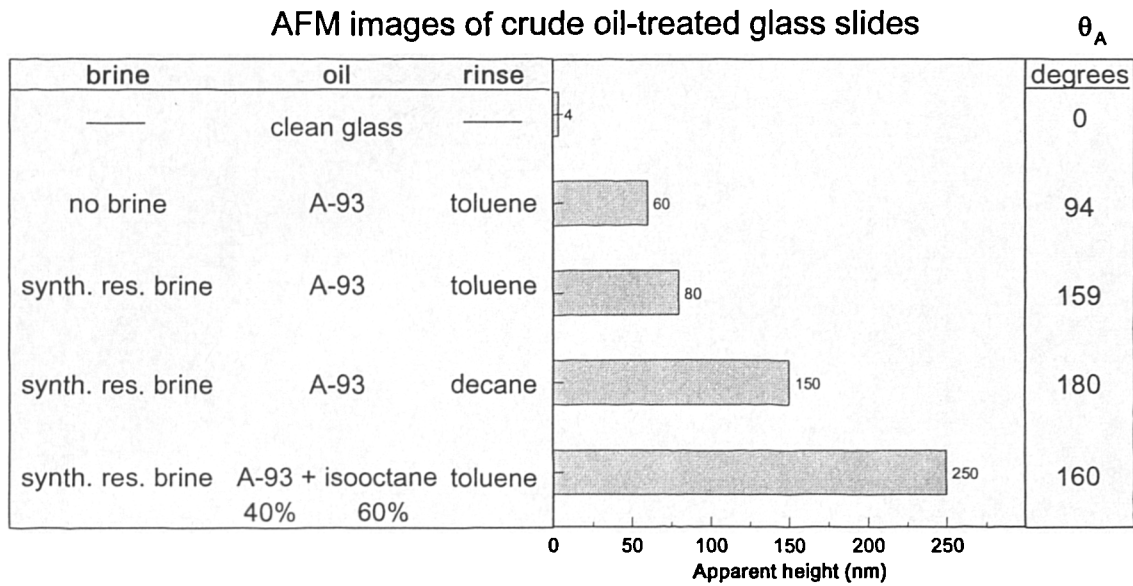


Figure 3-28. Apparent height of features observed by AFM varies with treatment of the surface. The maximum relief for images of $1 \mu\text{m}^2$ is shown for clean glass and for glass slides treated with A-93 crude oil. Variables include treatment of initially dry or wet surfaces, rinsing with toluene or decane, and alteration of the oil composition by addition of isooctane.

Fig. 3-28 shows the results the AFM measurements; Figs 3-29 through 3-33 are the AFM images. Clean glass surfaces were very flat (Fig. 3-29); for a $1 \mu\text{m}^2$ area, the maximum difference between the highest and lowest points was only 4 nm. Dry surfaces aged in A-93 crude oil for two weeks at 80°C , then rinsed with toluene, showed what appeared to be patches of adsorbed material covering about half of the surface (Fig. 3-30). A surface initially wetted with synthetic reservoir brine, aged in A-93 crude oil, and rinsed with toluene appeared to be covered with a fairly homogeneous texture of intertwined, cylindrically-shaped structures (Figs. 3-31). The height and diameter of individual cylinders are about 30 nm and they extend for much longer distances in their axial direction. In contrast, an identically treated surface washed with decane is covered with a layer of material that is less structured, with almost twice the apparent height (Fig. 3-32). Addition of isooctane to the oil phase gave the greatest height (250 nm on $1 \mu\text{m}^2$ of surface) of any of the surfaces examined (Fig. 3-33).

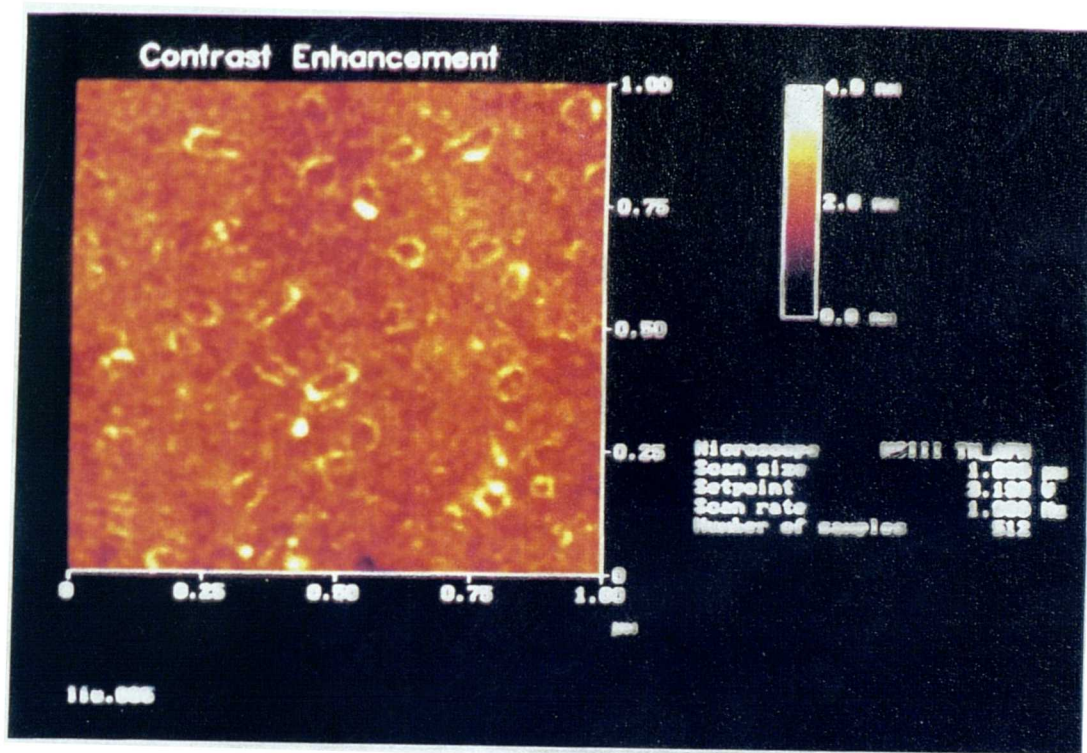


Figure 3-29. AFM image—clean glass surface.

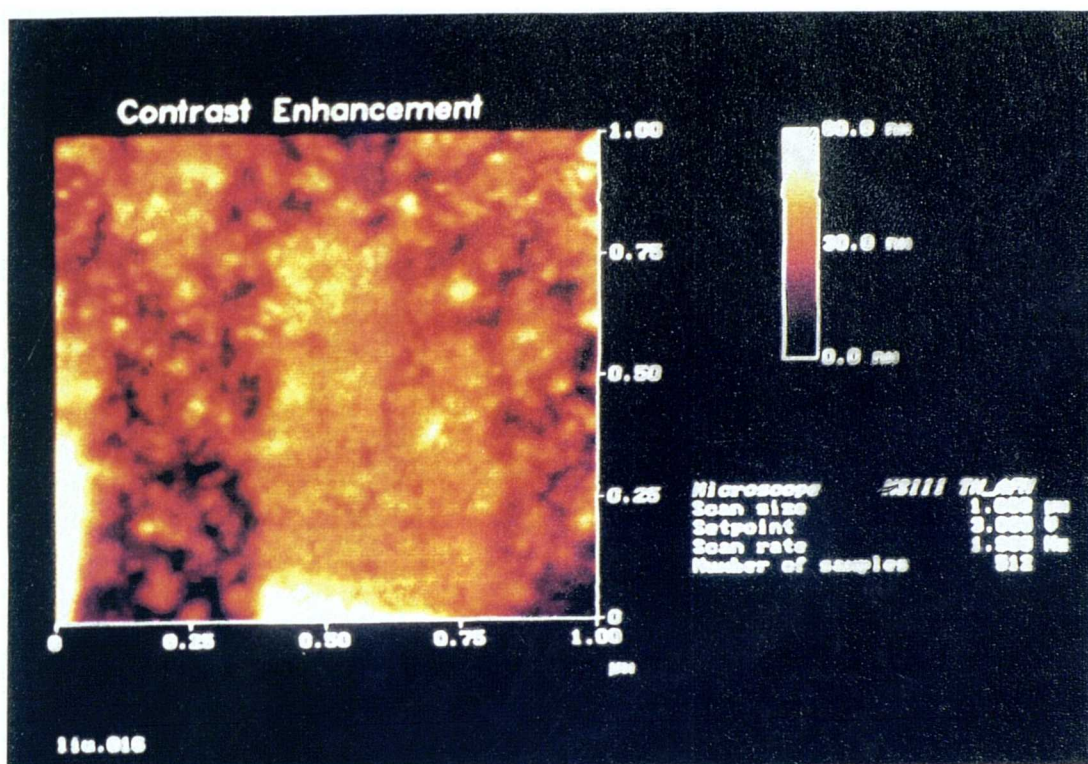


Figure 3-30. AFM image—dry glass surface aged in A-93 crude oil.

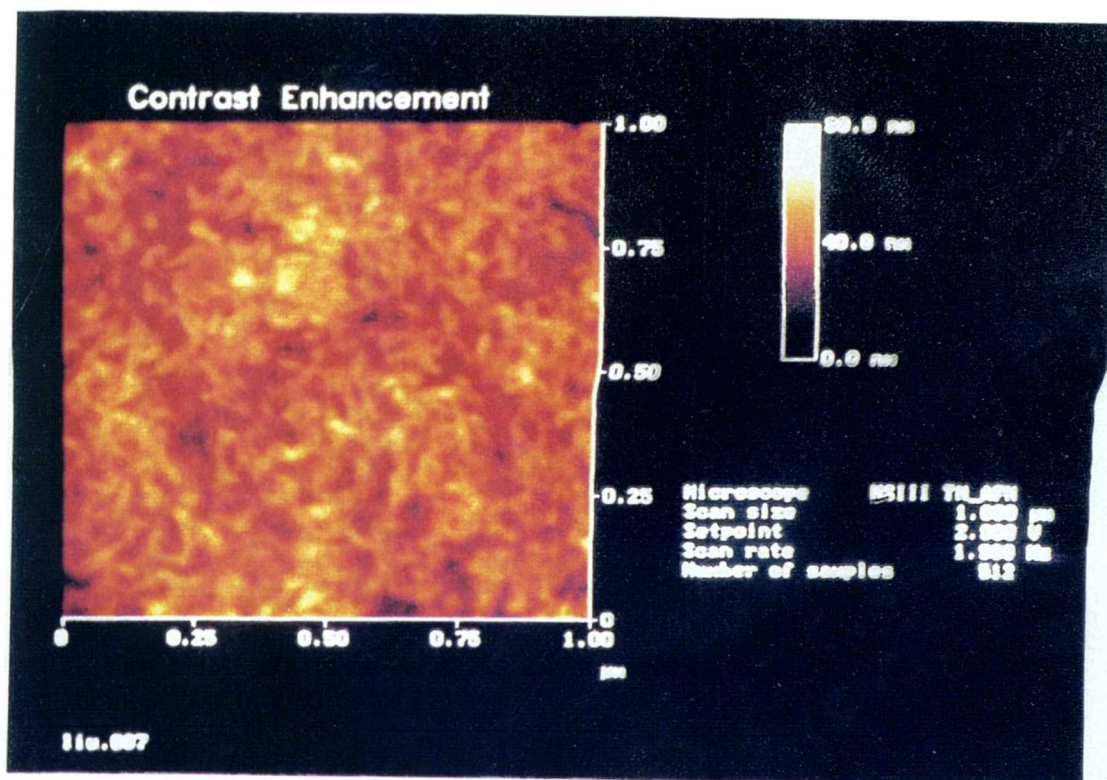


Figure 3-31. AFM image-wet glass surface aged first in synthetic reservoir brine, then in A-93 crude oil.

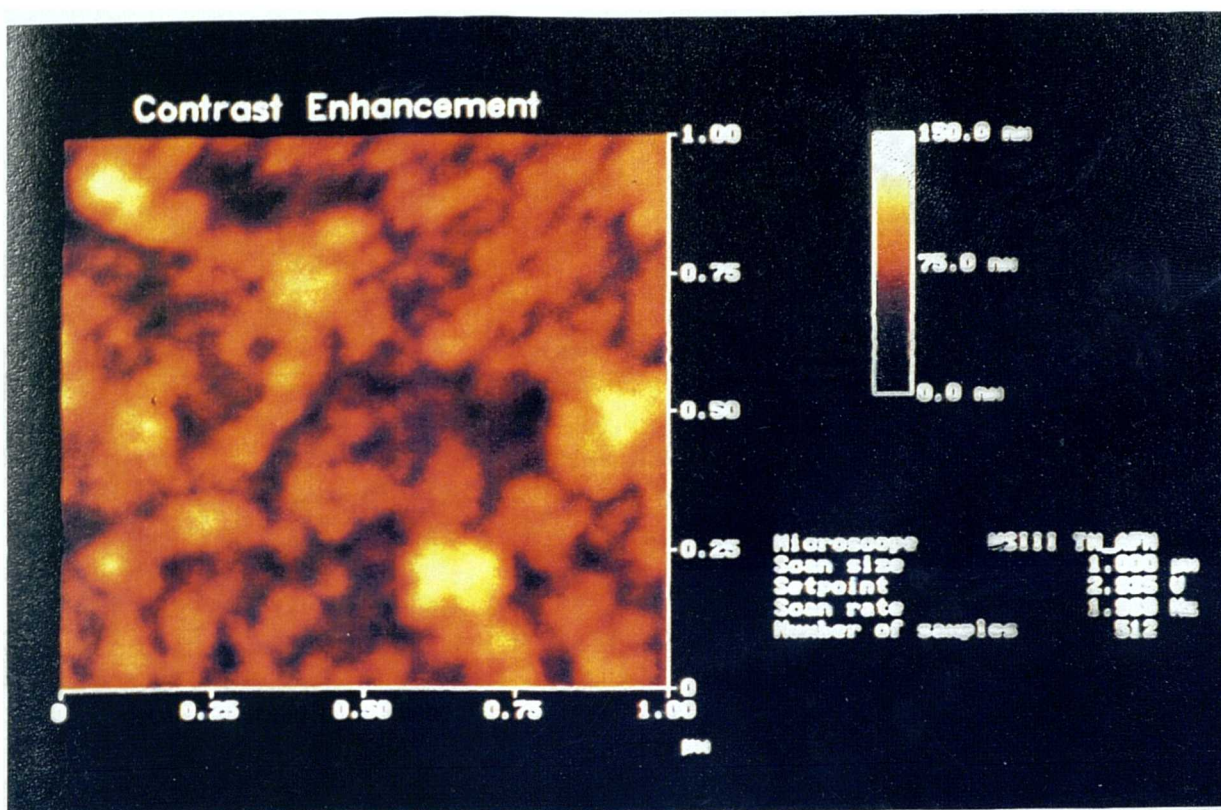


Figure 3-32. AFM image—wet glass surface aged in A-93 crude oil, washed with decane instead of toluene.

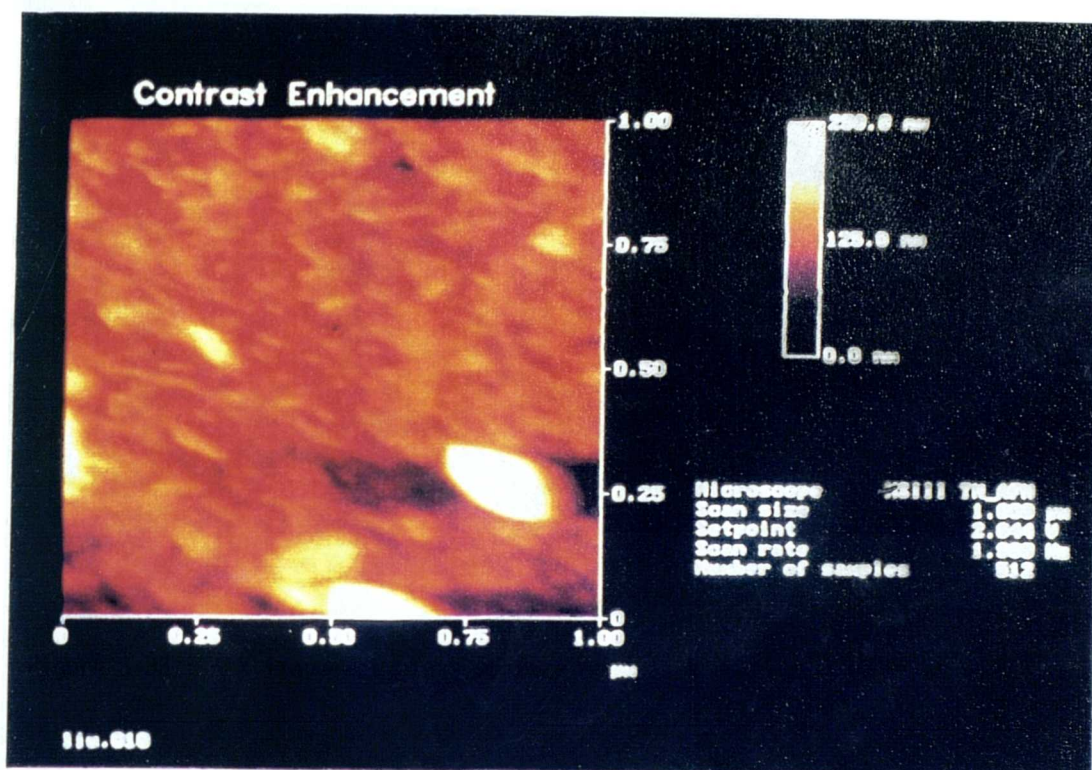


Figure 3-33. AFM image—wet glass surface aged in A-93 crude oil mixed with isooctane.

Conclusions

Wetting changes in oil reservoirs occur when components from crude oil adsorb on mineral surfaces. Close proximity of the compounds at the oil/brine interface to the solid surface emphasizes the importance of individual charged sites, over the net charge that controls interfacial phenomena including electrophoretic mobility. A key feature of crude oil/brine interfaces is that the interfacially active components can be either acidic or basic with negative or positive charge, respectively. Over a wide range of brine compositions, these interfaces often have both positively and negatively charged sites simultaneously. Interfacial tension falls with the transition from zwitterionic to negative sites only. For a particular crude oil and mineral surface, it is the composition of the brine between them that dictates the charge of their respective interfaces. Thus it is the brine composition (together with the capillary pressure) that determines whether a stable film of water can persist between the two interfaces and how thick such a film will be. If there is a stable thick film of water, adhesion does not occur. Strongly water-wet conditions can be maintained over geologic time, as demonstrated by the Athabasca tar sands.

If the water film is unstable, wetting alteration by adsorption of crude oil components can occur and adhesion is observed. Between unconditionally stable and unstable conditions, are combinations of oil, brine, and solid for which stability is conditional. The distinction between adhesion and nonadhesion can be shifted for these conditionally stable or metastable ensembles by changes in temperature or composition of the oil.

Changing composition of the oil by addition of either solvent or precipitant affects the size of asphaltene aggregates in solution. Adhesion is less likely for smaller aggregates because positive and negative interactions tend to balance one another. Larger aggregates maximize the opportunity for positive and negative sites to interact with the surface independently from one another. Addition of solvents to the oil reduces the tendency to adhere, whereas addition of precipitant increases adhesion.

Changing temperature can also affect the size of aggregates in the oil, with a similar effect on adhesion to that described for changing the oil composition. In tests with longer exposure times in oil, however, it appears that the kinetics of strong adsorption and rearrangement of adsorbed material—to give high contact angle surfaces that are resistant to toluene washing—can be accelerated by increasing the temperature. Thus temperature can play two, somewhat opposing roles.

Finally, the material that adsorbs on solids *from crude oil*, may, under some circumstances, be able to desorb. Wetting is a complex and dynamic feature of COBR ensembles. Identifying the mechanisms by which wetting is altered and the roles played by **all** of the components of the system may well permit the use of wettability control to maximize oil recovery.

Chapter 4

WETTABILITY ALTERATION IN POROUS MEDIA

Pore geometry, interconnectivity, surface chemistry of different minerals, and geological variability from one core sample to another all contribute to making studies in natural porous media more difficult to interpret with respect to wetting than those on flat glass or polished mineral surfaces. Nevertheless, the goal is to apply the principles developed in those simpler cases to interpretation of the alteration of wetting in rocks. The factors shown to affect crude oil/brine/interactions on flat surfaces, especially brine composition, are investigated in glass micromodels, and in consolidated cores of artificial and natural materials to show the relationships between wetting observations on flat surfaces and in porous media.

Introduction

In natural porous media, many complications are encountered when considering wettability alteration related to crude oil/brine/rock (COBR) interactions. The factors previously considered—oil and brine composition, surface chemistry, thermodynamic variables, and history of the entire system—remain influential. Superimposed on these are the chemical heterogeneity and surface roughness of minerals and considerable uncertainty regarding attainment of equilibrium in complex geochemical systems that may evolve very slowly. Serious obstacles remain in the way of reaching definitive answers about wetting *in situ* in that it can neither be preserved nor regenerated, with complete confidence, in rocks retrieved from subsurface formations.

One approach to the study of wetting *in situ* has been the use of transparent models in which the fluid distribution and pore filling sequences can be observed directly (for reviews see Buckley, 1991, and Wilson, 1994). In glass micromodels, the wetting of the high energy silica pore surfaces can be altered by interactions with crude oil components that should be similar to interactions reported on flat glass surfaces (Chapter 3). Some examples of the mixed wetting and displacement mechanisms that can develop are presented in a simple model with a repeating pattern of pores and throats.

As model porous media, micromodels are limited in several respects. The porous network is connected only in two dimensions and the scale of pore and throat sizes is

significantly different than in a typical reservoir sandstone. It is difficult to make quantitative measurements of pressures and volumes which are the main sources of information about the progress of displacements in cores and in the reservoir. To fill the gap between flat surfaces and reservoir rocks, a series of model porous media of increasing complexity has been selected for study including:

- a glass micromodel,
- Aerolith, a synthetic porous medium that is mostly silica, and
- Clashach and Berea Sandstones. Clashach is a relatively clean outcrop sandstone whereas Berea has a significant clay mineral content.

Brine compositions that give distinctly different wetting conditions on flat silicate surfaces have been selected to produce different wetting conditions for tests in this series of varying porous media.

Mixed Wetting in Glass Micromodels

The simplest porous medium tested consists of two plates of glass into which porous networks have been etched. The glass plates are fused together and inlet and outlet holes are drilled to intersect the porous network at either end.

Micromodel description

The dimensions of an etched glass model typical of those used for all the tests reported here are summarized in Fig. 4-1. The overall pattern consists of a network of larger open volumes or pores interconnected by four narrower etched tubes or throats. Intersections of throats, which are not etched out to form pores, are referred to as nodes. The square network of intersecting throats is oriented at approximately 45° to a straight line from the inlet to the outlet.

In cross section, the etched channels are characterized by having corners where the two glass plates are fused together. Pore size and shape parameters (area, breadth, long axis length, and perimeter) were acquired from videotaped records by image analysis techniques (software from Bioscan OPTIMAS). Average values of depth and width for pores, nodes and throats are included in Fig. 4-1. Throats were measured in the direction perpendicular to their individual axial directions; nodes and throats were measured in the direction perpendicular to a line from the inlet to the outlet. Estimated areas correspond well to the area calculated

for a pore formed by the intersections of circular arcs of the same depth and width dimensions.

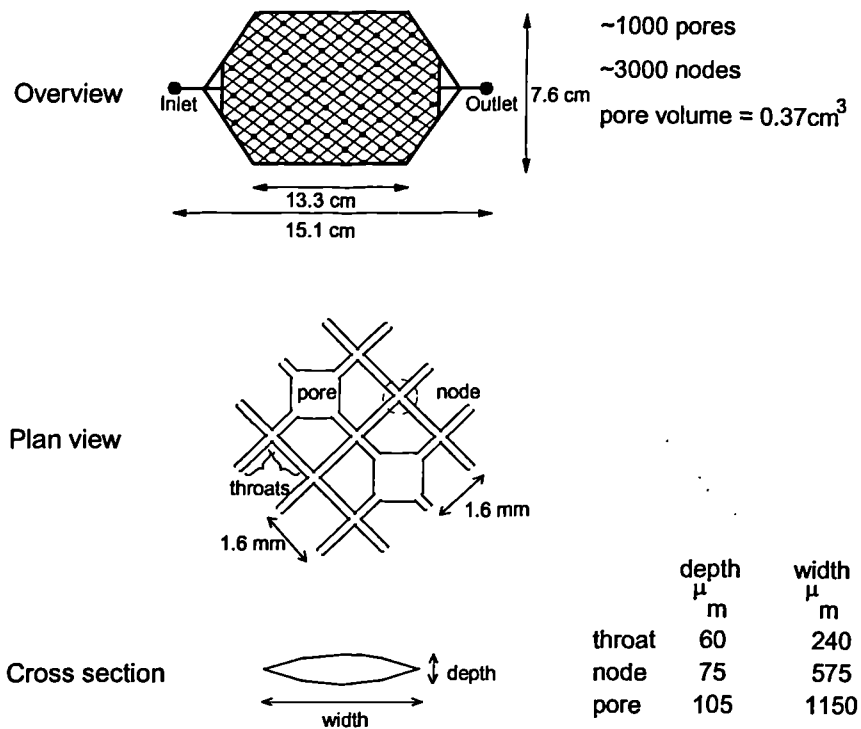


Figure 4-1. M-4 etched glass micromodel dimensions.

The same models were reused for multiple experiments, necessitating effective cleaning after exposure to crude oil. The models were cleaned by flushing with a succession of solvents including toluene and acetone, then treated with the standard hydrogen peroxide/ammonium hydroxide cleaning mixture, followed by flushing with copious amounts of distilled, deionized water. Finally, the model was heated for at least 48 hours at 450°C. Effectiveness of cleaning was tested by filling the model with distilled water, oil flooding with Soltrol 130, then observing a waterflood with distilled water. Snap-off in throats and trapping of oil in all the large pores is observed when the model is clean, demonstrating very strongly water-wet conditions, as illustrated in Fig. 4-2. This is quite a stringent test, since contact angles as low as 20 degrees can inhibit snap-off and trapping of the nonwetting phase (Wardlaw, 1982).

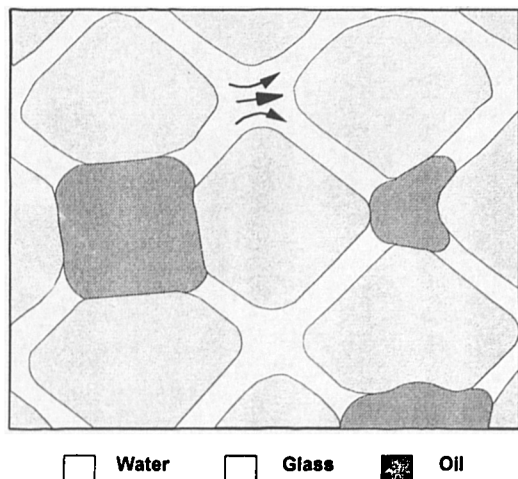


Figure 4-2. Waterflood of a mineral oil in a strongly water-wet micromodel.

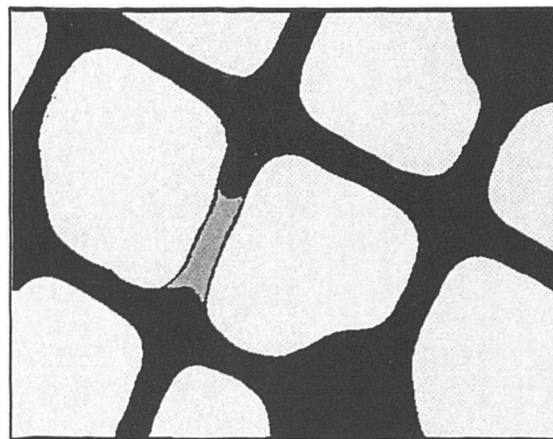
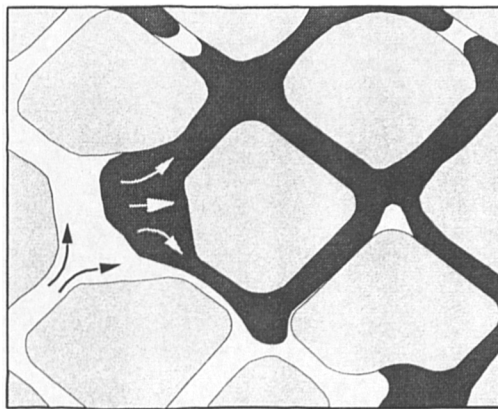


Figure 4-3. Residual water bridge after Moutray oilflood.

Mixed-wet displacement mechanisms

The trapping of nonwetting phase by snap-off is one displacement mechanism that has not been seen in any of the crude oil waterfloods observed in glass micromodels to date. The initial water-wet state of the model appears to be maintained during primary drainage. Mixed-wetting arises because water is the first fluid present and occupies corner wedges where the two etched glass plates were joined. In those corners, surfaces remain water-wet. Water bridges across throats connect the otherwise isolated wedges at the end of primary drainage. Such a bridge can be seen in Fig. 4-3; the associated wedges can be inferred from shrinking and swelling of the volume of water in the bridge as it is sucked into or supplied from wedges that often are not otherwise visible. Figs. 4-2 and 4-4 have been drawn to represent typical micromodel images whereas Figs. 4-3, 4-5, and 4-6 were digitized directly from videotape segments.

Adsorption of crude oil components can alter wetting in much of the model where there are thin films of water, but these changes are not evident until the start of the waterflood. The extent of wetting alteration depends on the nature of the oil, aging time and temperature, and brine composition, as discussed in Chapter 3. Judging from experiments on smooth glass surfaces, θ_A on surfaces contacted with crude oil probably can vary from about 30 degrees to nearly 180. Evidence for different mixed-wet displacement mechanisms with varying values of θ_A on the altered surfaces can be seen qualitatively in micromodel waterfloods.



Water
 Glass
 Oil

Figure 4-4. Very efficient mixed-wet waterflood.

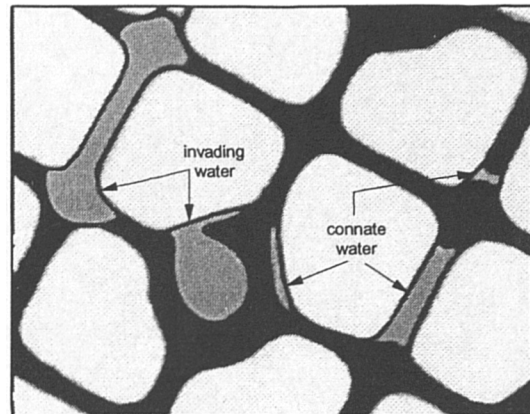


Figure 4-5. Displacement of Moutray by water flowing through corner wedges.

In mixed-wet systems where θ_A is relatively low, the oil/water interfaces are fairly flat as illustrated in Fig. 4-4. Stick/slip motion is common (suggesting that the effective value of θ_A is near 90 degrees). The oil phase remains well connected and displacement efficiency can be very high.

A case of mixed wetting with higher values of θ_A is shown in Fig. 4-5 where both invading and disconnected connate water are visible. Water flows through wedges to supply the bubble that is displacing oil from the large pore. An advancing angle of 110 degrees has been estimated, based on the shape of the growing water bubble, the cross-sectional shape of the pore, and constant curvature assumptions (Buckley, 1993b).

Some displacements appear to be oil-wet (Fig. 4-6) as indicated by the shapes of moving oil/water interfaces and by snap-off of the advancing water phase by the drainage mechanism described by Roof (1970). Crude oil displacements sometimes appear to be pseudo oil-wet in the sense that connate water wedges persist in the corners, but are isolated from invading flood water by persistent oil films. The presence of these water wedges is not apparent until the moment when an oil film breaks and invading water connects with connate water.

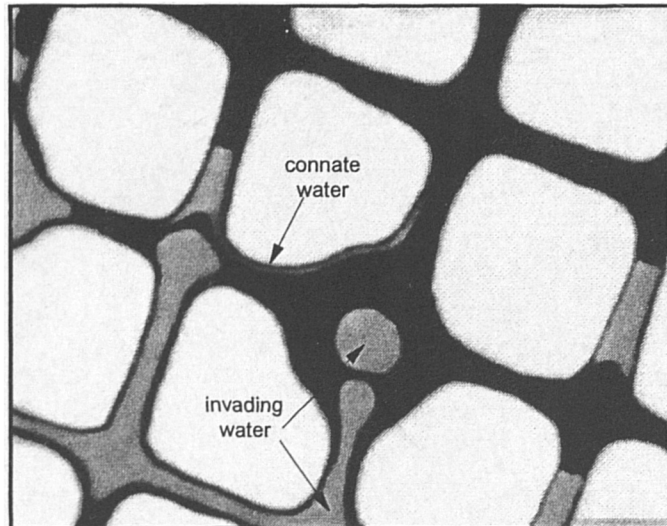


Figure 4-6. Oil-wet displacement of Moutray crude oil.

Using a simple model with a repeating pattern of high aspect ratio pores, it is possible to identify qualitatively a number of different displacement patterns, representing different mixed-wet conditions established by a variety of COBR ensembles. This suggests that different COBR combinations can also be used to create a variety of mixed-wet conditions in cores where more quantitative measures of wetting and oil recovery can be made.

Wettability Control Using a Crude Oil

The ideal experiment to test the effect of wetting on oil recovery would compare the results of otherwise identical corefloods that differ only with respect to wettability. How to do such an experiment, however, is not obvious. The problems that have been encountered fall into several categories:

- While strongly wetted models, either water-wet or oil-wet, can be achieved, they are probably not representative of wetting in many oil reservoirs.
- It is quite easy to change more than one variable at a time. Often changes attributed to wetting are at least partly due to altered permeability and pore geometry.
- COBR wetting shows cycle dependent hysteresis, as well as the more familiar drainage and imbibition hysteresis, increasing the difficulty of designing duplicate experiments.

In this study, mixed-wet conditions are generated by contacting porous media with an asphaltic crude oil (A-93) in the presence of selected brines. Aging time, aging temperature, oil composition, and initial water saturation, all of which can affect wetting,

were held as nearly constant as possible. The main variable in this study is the pH of the aqueous phase; compositions were chosen, based on smooth surface measurements, to maximize the impact on COBR interactions.

Influence of pH on COBR interactions

Reisberg and Doscher (1956) noted that exposing glass slides to water before submerging them in oil promoted oil/solid interactions. Rates of oil removal from the glass slides depended on pH of the water phase. Brown and Neustadter (1980) measured crude oil/brine/solid contact angles for solutions of varying pH and ionic composition. Water-wet conditions were observed with high pH and oil-wet with low pH or high salinity brines. The adhesion test was used by Valat *et al.* (1993) to characterize a French crude oil interacting with glass. Waterflood displacements from bead packs with pH 2 solution (adhesive conditions) produced less oil, and showed the early breakthrough and extended production that are characteristic of oil-wet conditions. A waterflood at pH 11 (nonadhesive conditions) was more typical of a water-wet displacement. IFTs were not reported, but may be significantly affected at these extremes of pH.

Skauge and Fosse (1994) used aqueous phase pH to vary wetting in Berea Sandstone exposed to a North Sea crude oil with 4.7% asphaltenes. Better oil recovery was observed for less water-wet conditions, consistent with the findings of Jadhunandan and Morrow (1995), but in contrast to the bead pack results of Valat *et al.* (1993).

The effect of pH on A-93 crude oil and its interactions with solid surfaces

Preliminary studies with A-93 crude oil on flat glass surfaces demonstrated the dramatic impact of varying solution pH on wetting. The adhesion map for borosilicate glass at 80°C (Fig. 4-7) shows a transition from adhesive to nonadhesive conditions between pH 4 and 6 for NaCl solutions of intermediate ionic strength (0.1 M). Adsorption on glass after treatment with pH 4 and pH 8 buffered solutions (shown in Fig. 4-8) confirms that very different wetting is established on surfaces aged in A-93, depending on the pH of the pretreating brine. (Details of the adhesion and adsorption experiments are given in Appendix B.)

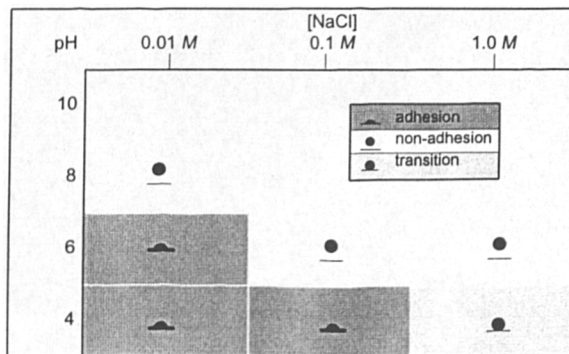


Figure 4-7. Adhesion of A-93 crude oil on borosilicate glass at 80°C.

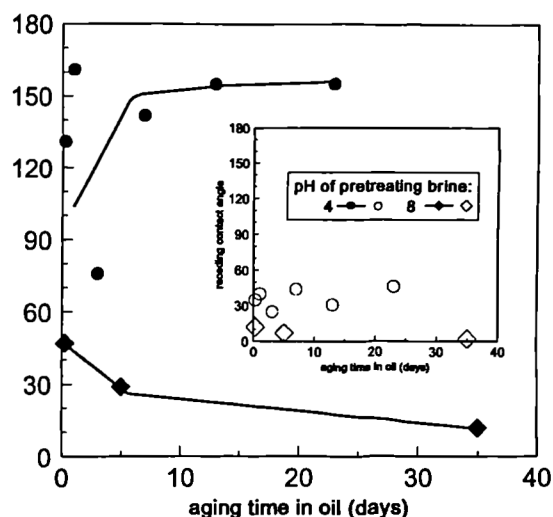


Figure 4-8. Alteration of wetting by adsorption from A-93 crude oil on borosilicate glass at 80°C.

Interfacial tension (IFT) between crude oil and brine can also vary with changes in pH and ionic strength of the aqueous phase, as discussed in Chapter 3. For many crude oils the decrease in IFT with increasing pH from 7 to 9 can be substantial (c.f., Figs. 3-13 and 3-14) and the very low tensions at high pH could have a major impact on oil recovery. Fig. 3-3 showed that IFT for A-93 varies only in the range of 20 to 25 dyn/cm with NaCl brines varying in pH from 4 to 10 and ionic strength from 0.01 to 1.0 M.

Controlled Wetting Experiments

The experimental COBR ensembles

Aqueous solutions: The brine phase was one of two low ionic strength solutions of 0.1 M NaCl. Solutions were buffered with either acetic acid (pH ≈ 4) or phosphate salts (pH ≈ 8). Water was distilled in glass; salts used were reagent grade. Brines were filtered (Millipore AP25 inline prefilter) and degassed prior to use in flow experiments.

Oils: The crude oil used to alter wetting is the asphaltic oil from Alaska (referred to as A-93). Light ends were evaporated from the crude oil under a vacuum before flow experiments to avoid formation of a vapor phase during corefloods. The oil was used without filtration; no plugging was observed during displacements with oil. This crude oil is of particular interest because it has been used in a number of different laboratory studies of

wettability alteration (Liu and Buckley, 1995; Mennella and Morrow, 1994; Ma *et al.*, 1994), and in a study of reservoir wetting (Jerauld and Rathmell, 1994).

Refined oils were used in measurements of strongly water-wet conditions (RO-1 and RO-2). A mixture (RO-3) of 20% toluene and 80% of a viscous paraffinic oil, formulated to avoid precipitation during mixing with A-93 crude oil, was used in imbibition and selected waterflood experiments. Based on previous experience, wetting conditions established during aging in crude oil are expected to be stable with time and not greatly affected by introduction of refined oil (Jia *et al.*, 1991).

Table 4-1 summarizes physical properties of the various fluids used in the porous media studies.

Table 4-1. Selected fluid properties (measured at 25°C)				
Fluid	Composition		Density (g/cm ³)	Viscosity (cp)
low pH brine	pH =4	[Na ⁺] = 0.1M	1.0026	0.916
high pH brine	pH =8	[Na ⁺] = 0.1M	1.0051	0.956
A-93 (cyl. 1)	10.7% asphaltenes		0.9016	52*
A-93 (cyl. 2)	(asphaltenes not measured)		0.9025	70*
RO-1	Soltrol 220 (mixture of C ₁₀ - C ₁₃ paraffins)		0.7774	3.6
RO-2	180-190 Saybolt Viscosity Paraffin Oil (SVPO)		0.8628	87.8
RO-3	1/5 toluene + 4/5 SVPO		0.863	11.5

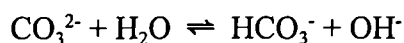
* measured after evaporation of light ends.

Porous media: The micromodel pattern described above was used to test both combinations of A-93 and brine, with aging conditions matching those in the cores.

Berea Sandstone has traditionally been the standard model sandstone for laboratory coreflood studies. Waterfloods in Berea have therefore been included in this study, despite concerns that isolation of the effects of wetting alteration might be frustrated by rock/brine interactions. These interactions include

- alteration of the pH of injected brine
- mobilization of fines
- changes in surface chemistry and surface charge.

Alteration of the pH of injected brine was demonstrated by Kia *et al.* (1987). Berea sandstone contains a small percentage of carbonate minerals. Dissolution of calcite, for example, produces CO_3^{2-} ions which raise solution pH by hydrolysis of water:



Depending on the salinity, pH of the effluent was increased as much as 3 units over that of the injected brine. Less drastic buffering effects were observed in the Berea Sandstone samples tested by Jadhunandan (1990).

Mobilization of fines can occur when repulsive electrostatic forces between clays and the solid surfaces of the matrix dominate over the attractive van der Waals forces. The repulsive forces vary with pH and ionic strength of injected aqueous solutions. According to Kia *et al.* (1987), repulsive forces between fines and pore walls dominate in Berea if the concentration of monovalent salts is less than 0.014 M at pH 4.5 or less than 0.038 M at pH 8.6. According to these guidelines, fines migration should not occur in either of the salt solutions used in this work, although some variability in Berea samples can be expected. For example, Khilar and Fogler (1984) reported core damage below an NaCl concentration of 0.071 M for unbuffered solutions (pH was not reported).

Dissolution of calcite and other minerals also provides a source of multivalent ions that affect the surface charge of both the solid/brine and oil/brine interfaces. Depending on the specific minerals involved, greater dissolution could occur under more acidic or more basic conditions.

Because of the recognized potential for brine/rock interactions in Berea, two additional porous media, one synthetic and the other a clean sandstone, were selected for this study. Aerolith-10 is a synthetic silicate material that has been used by other researchers as a model porous medium (Hamon and Vidal, 1986; Gauchet, 1993). Clashach Sandstone, from an outcrop in Scotland, has much less clay than Berea. Clashach also has been used frequently in laboratory studies (Todd *et al.*, 1988; Naylor *et al.*, 1991), including tests of scale inhibitors over a range of aqueous phase pH (Jordan *et al.*, 1994).

2" (5 cm) long cores of 1.5" (3.8 cm) diameter were cut from one block of Aerolith-10, two different blocks of Clashach, and one of Berea sandstone. X-ray fluorescence analysis of Aerolith showed that it is composed of 91% silica, 4% alumina, and minor amounts of other oxides and trace metals. Petrographic analyses of Clashach and Berea are

shown in Table 4-2; core dimensions and properties of individual core samples are in Table 4-3, which summarizes the conditions and major results of all of the tests performed.

Table 4-2. Petrographic analyses of Clashach and Berea sandstone.			
Core Labels	Clashach		Berea*
	K#	L#, M#	Q#
Average K_{N_2} (md)	700	1400	1100
Porosity (ϕ , %)	18	20	22
Petrographic analysis:			
Quartz	60.4 %	64 %	78.5 %
Quartz cement	15.5	10.4	
Feldspars	4.3	4.6	6.0
Rock fragments	2.5	7.8	8.6
Dolomite			2.5
Chert			1.6
Kaolinite			2.8
Porosity	15.3	12.8	18.3

* from Ma and Morrow, 1994

Core preparation

Brine composition is only one of the factors that influences COBR wetting alteration with a given crude oil. Other factors, including aging temperature and aging time, have been chosen, based on results of the preliminary flat surface tests to maximize the differences in wetting achieved. These tests on surfaces pretreated with brine, over a range of ionic compositions, aging temperatures and time (Liu, 1993) usually showed consistent advancing contact angles after about two weeks of aging in crude oil at 80°C (for example, see Fig. 4-8).

Core preparation was therefore standardized to include both the brine pretreatment and crude oil aging steps. Cores were first equilibrated at room temperature with 100% brine saturation. After soaking in brine for a week, additional brine (at least 20 PV) was flushed through the cores and, for the core plugs listed in Table 4-4, effluent pH was monitored for the first four pore volumes produced. Very little change in pH was observed for either high or low pH cases in any of the porous media tested.

Core material	Core ID	L (cm)	A (cm ²)	K _{Hz} (md)	K _{mine} (md)	φ (%)	Brine pH	Oils		Flow rate (cm ³ /hr)	V _{front} (ft/day)	S _{wf} (%)	K _c (S _{wf}) after aging (md)	S _{or} (%)	BT[or imb] Rec. (%OOIP)	Final WF Rec. (%OOIP)	I _w	I _b
								Aged in	Tested in									
Aerolith-10	A2	4.43	10.1	4810	1510	43.5	8	A-93	A-93	4.3 70	1.15 18.9	18.1 23.5	3600 3000	11.8 9.9	35.4 23.1	85.6 87		
	A3	5.61	10.2	4500	1390	43.3	4	A-93	A-93	4 70	1.41 20.1	18.8 16.5	1510 1750	30.8 21.4	21.9 8.22	63.3 74.4		
	A3-CI	5.69	10.2	4090	2670	42.5	8	A-93	RO-3	54	17.1	17.9	3225	24.7	21.6	70		
	A4	5.14	10.1	4340	1960	44.5	8	A-93	RO-3			21	3800	14.3	[81.9]	81.9	1.0	0
	A5	5.98	10.2	4725	1860	45.0	4	A-93	RO-3			18.6	3480	25.6	[33.7]	68.6	0.49	0
Berea	Q70	6.33	10.2	1060	270	21.4	4	A-93	A-93	4.5 70	2.3 53.3	21.5 33.0	74 70	20.0 19.9	31.0 5.4	74.0 70.3		
	Q71	5.31	10.2	1100	267	22.2	8	A-93	A-93	4.3 70	3.9 75.2	19.7 30.1	350 660	41.6 37.5	6.7 14.9	48.1 46.3		
	B300-5	7.10	10.1	910	546	21.8	4	A-93	RO-3			27.2	361	24.5	[16.7]	65.8	0.25	0.11
	B300-3	7.43	10.1	937	469	22.7	8	A-93	RO-3			31.5	293	23.3	[28.2]	66.0	0.43	0.08

Table 4-3. Summary of core tests.

Core material	Core ID	L (cm)	A (cm ²)	K _{Hz} (md)	K _{brine} (md)	φ (%)	Brine pH	Oils		Flow rate (cm ³ /hr)	V _{front} (ft/day)	S _{wi} (%)	K _c (S _{wi}) after aging (md)	S _{or} (%)	BT[or imb] Rec. (%OOIP)	Final WF Rec. (%OOIP)	l _w	l _o
								Aged in	Tested in									
Clashach	K1		10.2	840	221	18.3	4		RO-1	13 130	26.7 36.6 422	26.7 33 40	440 524 440	50.1 52 47	5.5	31.6 24 22	1.0	0
	K2	4.83	10.2	660	141	18.5	4	A-93	A-93	4.5 70	4.9 91.3	25 35	230 290	37 33	32.1 30.3	49.3 48.8		
	K2-CI	4.81	10.2	680	425	18.6	4	A-93	RO-3	50	39.4	29	350	25.7	36.9	63.8		
	K3	5.4	10.2	590	178	18.3	8	A-93	A-93	4 70	3.5 91.4	38 55	500 700	13.2 12.7	19.3	78.7 71.6		
	K3-CI	5.4	10.2	461	320	18.25	8	A-93	RO-3	51	39.4	36	650	9.3	51.5	85.5		
	L1	6.09	10.1	1450	607	19.6	4	A-93	RO-3			22.5	788	40	[21.0]	48.7	0.43	0.5
	L2	6.47	10.2	1452	654	19.7	8	A-93	RO-3			28.9	990	18	[24.5]	74.7	0.33	0.18
	L3	6.48	10.2	1341	543	19.2	4	A-93	RO-3	4	5.3	24.1	665	45.5	34	40		
	L4	6.44	10.2	1406	652	19.5	8	A-93	RO-3	4	3.0	34.2	710	12.5	33.3	81		
M3	6.68	10.2	1725		20.0	8		RO-2			21.2							
M4	6.67	10.2	1717	1483	19.6	4		RO-2			19.6							
M9	5.9	10.1	1345	711	19.9	8	A-93	RO-3	4	3.3	30.9	1029	21.3	42.6	69.2			

Table 4-4. pH of effluent brine.						
Core Material	Core ID	pH (injected)	pH (produced)			
			1st PV	2nd PV	3rd PV	4th PV
Aerolith-10	A3	3.9	4.1	4.0	3.9	-
Aerolith-10	A2	8.0	8.3	8.0	8.0	8.0
Clashach	K1	3.9	4.0	3.9	3.9	-
Clashach	K2	3.9	4.1	3.9	3.9	-
Clashach	K3	8.0	7.9	7.9	8.0	8.0
Berea	Q70	3.9	4.3	4.3	4.1	4.1
Berea	Q71	8.0	8.1	8.0	8.0	8.0

Brine was displaced by crude oil, followed by two weeks of aging in the oil (with connate water) at 80°C. After cooling to room conditions, aged oil was replaced by either fresh crude oil or RO-3 refined oil mixture. (Additional details of standard procedures used in waterflood and imbibition tests are provided in Appendix E.)

Micromodel waterfloods

Waterflood tests were performed in glass micromodels following the same sequence of treatments and displacements as in waterflooding cores. After saturation with either the high or low pH brine, the model was allowed to equilibrate for one week at room temperature. The first displacement was a primary drainage with A-93 crude oil, after which the model was sealed and aged for a minimum of two weeks at 80°C. The subsequent waterflood, at a rate of 1 ml/hr, was recorded on video tape. Oil displacement efficiency was estimated after waterflooding by counting pores from which oil has been partially or completely swept; results are shown in Fig. 4-9. With the pH 4 fluid, more bypassed oil remains in the pores and nodes of the model and thus recovery is poorer than in a comparable test with pH 8 solution. Wettability was not measured directly, but can be judged qualitatively from the shapes of moving interfaces and from observed displacement mechanisms. Neither high nor low pH waterflood appeared to be strongly water-wet.

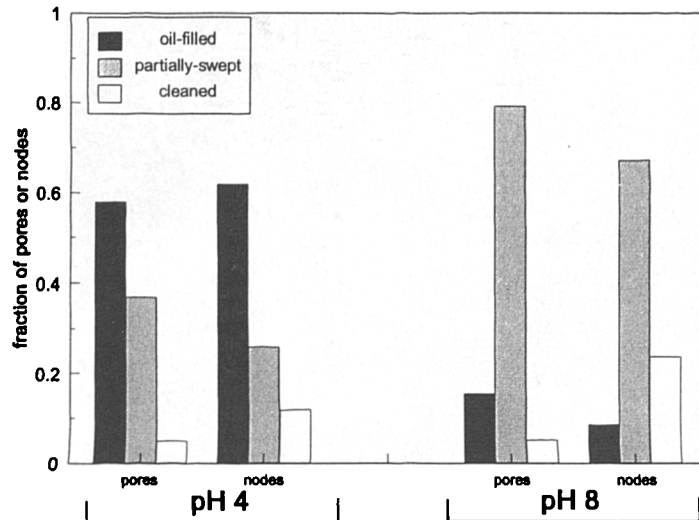


Figure 4-9. Results of waterfloods of micromodel aged in A-93 crude oil at 80°C for 2 weeks.

Aerolith-10 synthetic cores

Imbibition: The rates of imbibition into Aerolith cores, after aging in A-93, are shown in Fig. 4-10. Data for the strongly water-wet case are included (Hamon and Vidal, 1986). The inset compares the same three sets of imbibition data plotted as a function of dimensionless time (Zhang *et al.*, 1995):

$$t_D = t \sqrt{\frac{K}{\phi}} \frac{\gamma}{\sqrt{\mu_o \mu_w}} \frac{1}{L_c^2}$$

where t is the imbibition time, K is permeability, ϕ is porosity, γ is the interfacial tension, μ_o and μ_w are the viscosities of oil and brine, respectively, and L_c is a characteristic length that depends on core geometry and configuration of the surfaces exposed to the imbibing phase.

The sharp distinction between the water imbibition rates for these three conditions is evident in both the unscaled and scaled plots. Both high and low pH cases imbibe water more slowly than the strongly water-wet example. There is, in addition, a significant difference in the wetting conditions established in these two cases, with high pH being more water-wet ($I_w = 1$) and the low pH less water-wet ($I_w = 0.5$). Very little oil imbibes into either of the crude oil-treated cores.

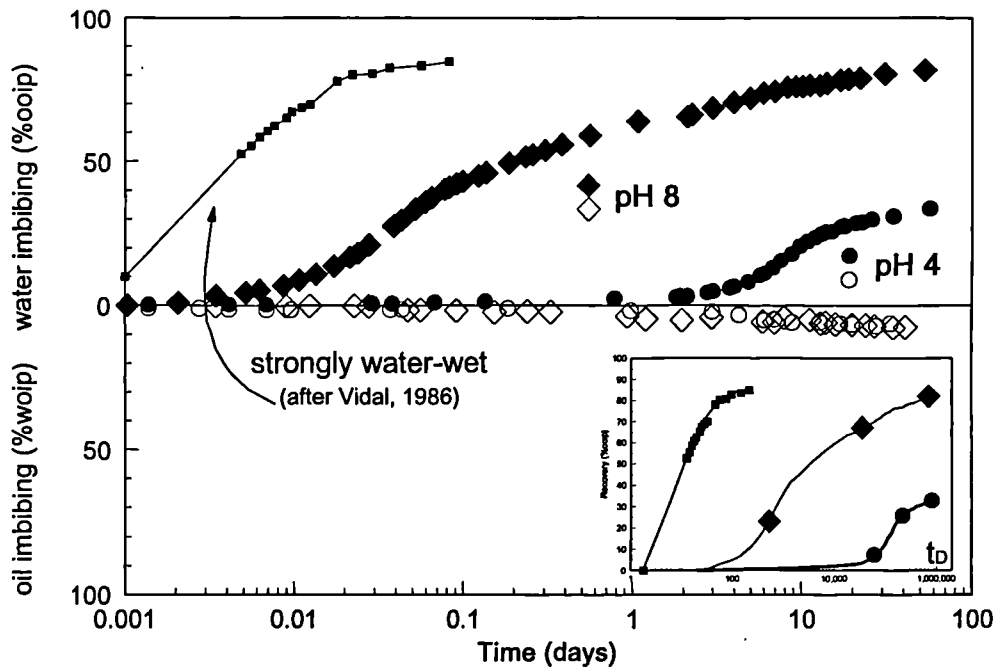


Figure 4-10. Imbibition into Aerolith-10 cores aged in A-93 crude oil at 80°C for 2 weeks.

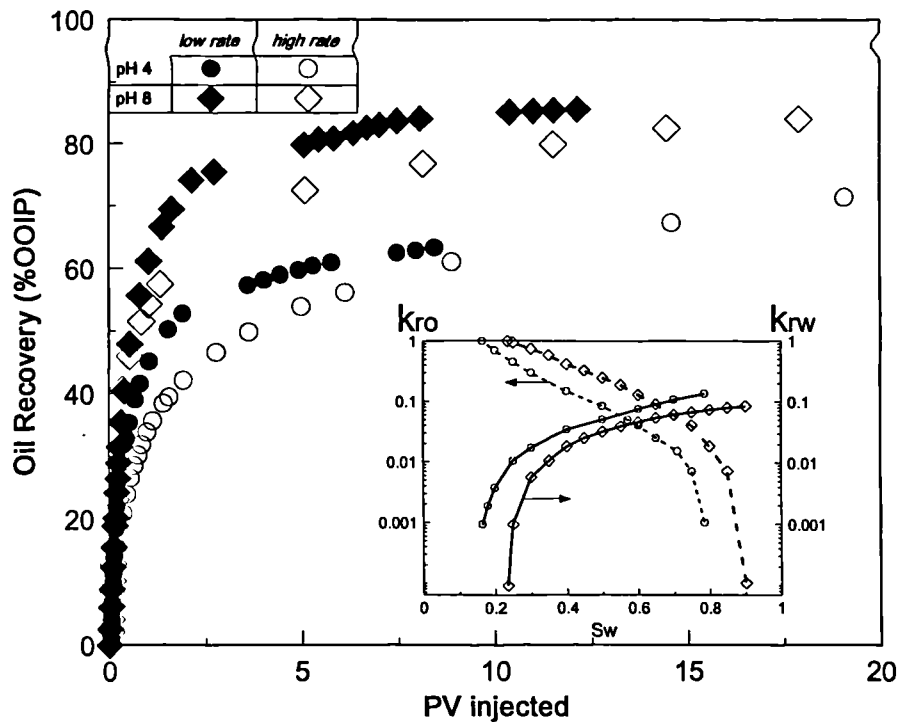


Figure 4-11. Low and high rate waterflood production histories from Aerolith-10. Inset shows the relative permeabilities calculated from the high-rate flood oil production and pressure data.

An Amott index to water of 1 is normally considered strongly water-wet; differences in imbibition rate, such as those shown in Fig. 4-10 are not considered in standard wetting evaluations which compare only end-point saturations. This lack of discrimination of the Amott index in the weakly water-wet range has been pointed out by Morrow *et al.* (1994) and Zhou *et al.* (1996). The rate of water imbibition is particularly sensitive to distinctions in wetting in the water-wet to weakly water-wet range. Over this range, major changes in displacement efficiency can be observed because of changes in displacement mechanisms, as discussed later in this chapter.

Wetting alteration in the synthetic silicate cores is consistent with wetting alteration on similar flat surfaces. The differences in water advancing contact angles between the high and low pH cases measured on flat silicate surfaces are translated into more and less water-wet conditions, not water-wet and oil-wet, as might be expected on the basis of the absolute values of those contact angles. This behavior may be related to the development of mixed wetting, i.e., only some fraction of the surface is exposed to contact with the oil, while the remainder of the surface is protected by water. Since no oil imbibes, we can infer that continuous oil-wet pathways have not been formed. Another factor may be the acid/base interactions that account for wetting alteration of Aerolith by A-93 in the presence of NaCl brines. These interactions can be reversible. Mechanisms by which oil components interact with various surfaces, the strength and possible reversibility of those interactions, will be discussed in Chapter 5.

Oil recovery by waterflooding: Results of waterfloods in crude oil-aged Aerolith cores at two flow rates appear in Table 4-3 and Fig. 4-11. After a low rate flood (about 1 ft/day), the cores were reflooded with oil, followed by a second waterflood at a rate about 20 times higher than the first. In the high-rate floods, the influence of capillary forces is minimal and estimates of relative permeabilities to water and oil (k_{rw} and k_{ro} ; inset to Fig. 4-11) were obtained from history matches to production and pressure data using a one-dimensional coreflood simulator. Relative permeability curves for pH 4 are shifted toward lower saturations and the end-point k_{rw} is higher, consistent with less water-wet conditions. The high pH flood was significantly more efficient in recovering oil (87% OOIP) than the low pH flood (74% OOIP). Extended production was observed to some extent in all of the waterfloods, but was more pronounced for the low pH and high rate floods.

Clashach sandstone cores

Primary drainage: After equilibration with pH 4 and 8 brines, cores were flooded with A-93 crude oil. The aim was to match initial water saturations as closely as possible, since the extent of wetting alteration can vary with S_{wi} for otherwise identical fluids and aging conditions (Jadhunandan and Morrow, 1995). No difficulty was anticipated since, except for the pH of the brine, the fluids used were identical. In Aerolith, values of S_{wi} were comparable for the low and high pH cases, but in Clashach the resulting values of S_{wi} were distinctly different, depending on the solution pH (Fig. 4-12).

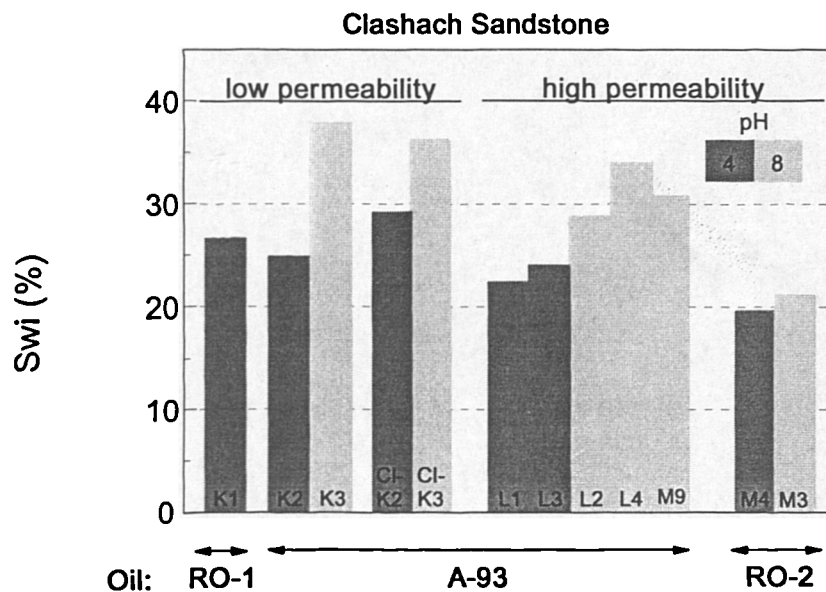


Figure 4-12. S_{wi} varies with pH of the brine being displaced in Clashach sandstone.

Clashach cores, regardless of permeability, had consistently higher water saturations after primary drainage if they were treated with pH 8 solutions before flooding with A-93 than did cores equilibrated with the pH 4 solution. In contrast, cores flooded with RO-3 mineral oil reached similar values of S_{wi} , regardless of brine pH. Since IFT is changed only slightly and other fluid properties are essentially identical, it seems likely that there is a significant difference in wetting during primary drainage with crude oil, even before the aging step.

Mineral oils which lack surface active components do not alter wetting. Thus the two oilfloods with refined oil (M3 and M4) have similar end-points. In these strongly water-wet tests, a more viscous oil was used, resulting in a higher capillary number for the displacement and thus a reduced value of S_{wi} (Al-Fossail and Handy, 1990).

Correlation between contact angles and uniform wetting has been demonstrated for low energy surfaces (Morrow and McCaffery, 1978). For primary drainage, lower values of S_{wi} are observed as contact angles increase. The water receding contact angles, θ_R , in COBR systems are probably low. Receding angles for the fluids in this study on glass surfaces differ significantly as a function of pH. When the brine has a pH of 4, θ_R is 50 degrees; for brine of pH 8, θ_R is only 10 degrees. Differences of similar magnitude were found in adsorption tests after several weeks of aging (inset to Fig. 4-8).

Imbibition: Aging in A-93 for two weeks at 80°C altered wetting of both the pH 4- and pH 8-treated Clashach cores, as shown by the imbibition rates in Fig. 4-13. Wettability alteration in these cores is quite different than in Aerolith, where a clear distinction between pH 4 (less water-wet) and pH 8 (more water-wet) was found. In Clashach, mixed wetting is generated by aging in A-93 crude oil with either of these low ionic strength NaCl brines. The core treated with pH 4 solution is more oil-wet. Either low pH or low S_{wi} (or a combination of both) could be responsible for making this case more oil-wet.

Oil recovery by waterflooding: A total of nine waterfloods were conducted in five Clashach core plugs after aging with A-93 crude oil. Core properties, initial conditions, and waterflood results are included in Table 4-3. Where more than one waterflood is indicated for a given core, tests were performed in the order in which they are listed in the table. Fig. 4-14 shows the results of three waterfloods in low and high permeability Clashach samples, all with the pH 8 solution as the brine phase. Displacement efficiency is similar for the high and low permeability core samples.

In cores K2 and K3, the initial low-rate waterflood was followed by a second drainage with oil and another waterflood at higher rate. Although the high and low rate displacement efficiencies were similar, it is not clear that these are meaningful comparisons. Significant differences in S_{wi} achieved during primary and secondary drainage illustrate the trapping of water that occurs after wetting has been changed by aging in crude oil (Salathiel, 1973).

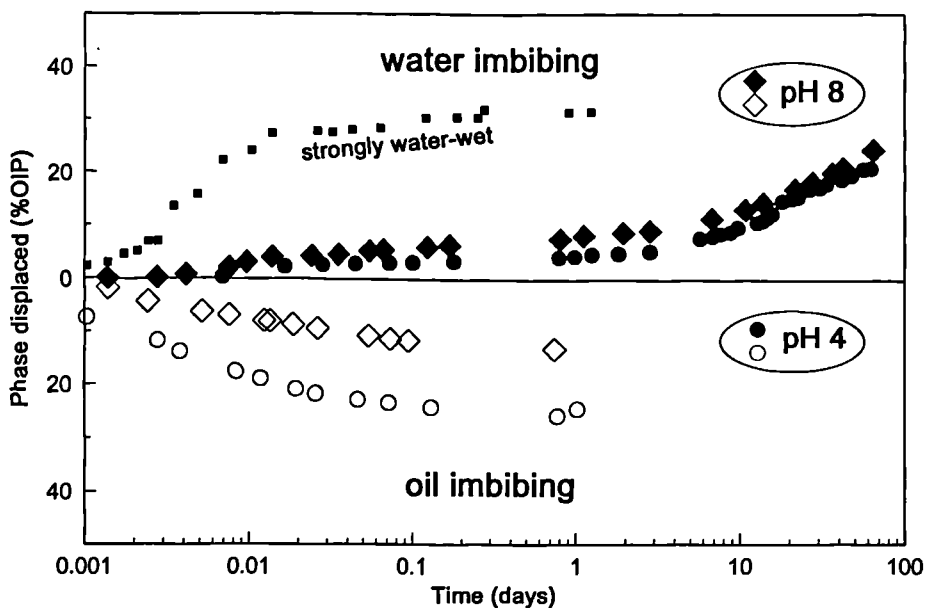


Figure 4-13. Imbibition into Clashach sandstone cores aged in A-93 crude oil at 80°C for 2 weeks.

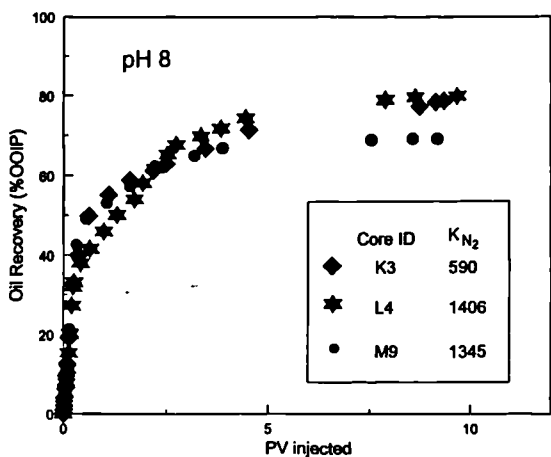


Figure 4-14. Low rate waterflood recoveries from Clashach sandstone of different permeabilities.

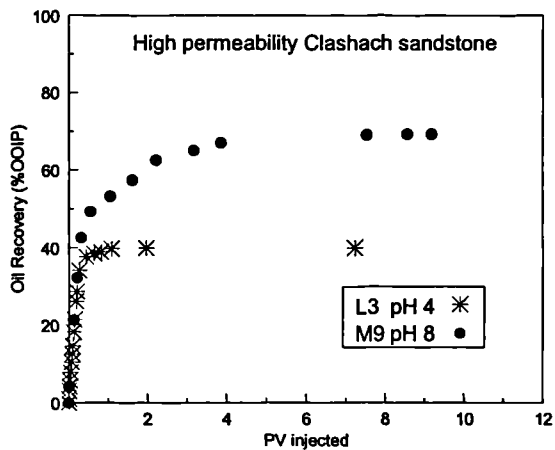


Figure 4-15. Low rate waterflood recoveries from Clashach Sandstone (varying pH).

One way to circumvent this problem is to clean the cores and repeat the aging step. Cores K2 and K3 were cleaned with toluene and isopropanol, then aged in A-93 crude oil. Cleaned cores had higher permeabilities to both brine and oil than did either core originally. Recovery efficiencies were significantly higher as well. Thus sequential tests in a single plug, with or without cleaning and restoring, were unsuccessful in duplicating the conditions established during primary drainage and aging of the cores. These experiments are better duplicated in matched cores. The plugs are never exact duplicates, but the problems of cycle-dependent hysteresis (Hawkins and Bouchard, 1992) and irreversibility of the wetting alteration can be avoided.

Because of the differences in S_{wi} between cores treated with pH 4 and 8 brines, comparisons between the waterflood results are not straightforward. The closest comparison is for two of the high permeability cores, L3 and M9, as shown in Fig. 4-15. Displacement efficiency is clearly higher in the less oil-wet (pH 8) case. In part, this occurs because S_{wi} is higher, so the total volume of oil initially in the core is reduced, but the volume of oil displaced is also higher for the less oil-wet of these two waterfloods.

Berea sandstone cores

Imbibition: Tests of spontaneous imbibition of water and of oil were conducted with Berea and pH4 and 8 brines. The results, shown in Fig. 4-16, indicate that in both cases, the cores became mixed-wet. More water and more oil imbibe into the core treated with the higher pH brine.

Oil recovery by waterflooding: The results of high- and low-rate waterfloods are shown in Fig. 4-17. The trends of oil recovery with pH are the reverse of those observed in Aerolith and Clashach. Better recovery is clearly demonstrated in the pH 4 waterflood and very poor displacement efficiency in the pH 8 test, in agreement with Skauge and Fosse (1994). The high-rate waterfloods in Berea are again not comparable to the low-rate floods because initial water saturations were consistently and substantially higher on secondary drainage than they had been for primary drainage (Table 4-3).

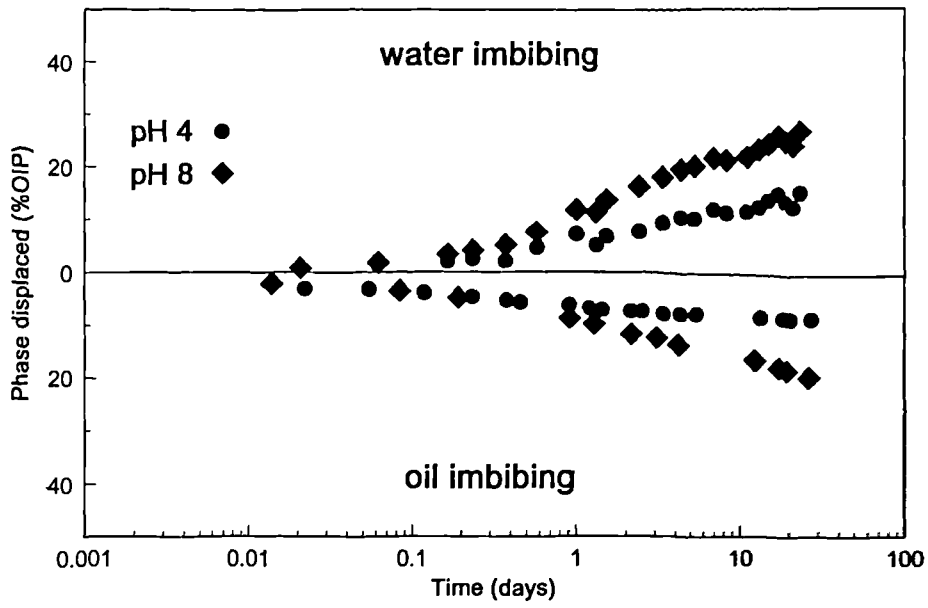


Figure 4-16. Spontaneous imbibition into Berea sandstone after aging in A-93 crude oil for 2 weeks at 80°C.

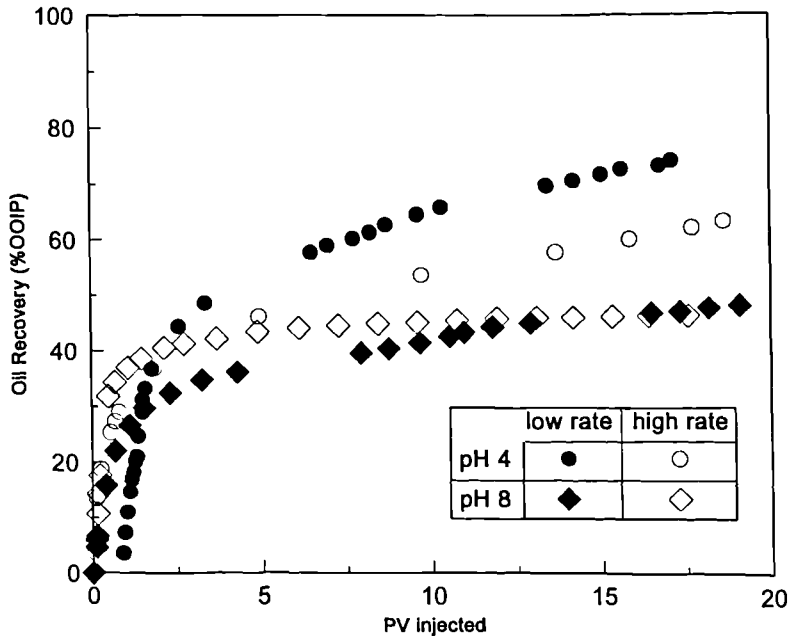


Figure 4-17. Waterflood recoveries from Berea Sandstone (varying pH and flow rate).

Summary of imbibition and waterflood results

Some of the core test results were surprising, both in terms of the wetting alteration achieved and the effect on oil recovery efficiency by waterflood. As shown in Tables 4-5 and 4-6, COBR wetting effects varied with both brine and core type. These results do not contradict previous studies, but they do point out the need for a careful reexamination of the generality of interpretations based on assumptions about wetting.

	Aerolith		Berea		Clashach	
	pH4	pH8	pH4	pH8	pH4	pH8
I_w	0.49	1.00	0.25	0.43	0.43	0.33
I_o	0.00	0.00	0.11	0.08	0.50	0.18
I_{w-o}	0.49	1.00	0.14	0.35	-0.07	0.15

	Aerolith	Berea	Clashach
low rate	pH4 < pH8	pH4 > pH8	pH4 < pH8
high rate	less oil recovered for same PVI	pH4: less than low rate pH8: more than low rate (up to 10 PVI)	differences in S_{wi} make comparisons uncertain

Influence of Core Composition on Wetting Alteration

Carbonate and siliclastic rocks have very different surface chemistry and should experience distinctly different wetting alteration with the same crude oil. While the importance of carbonate rocks is recognized, they are beyond the scope of this work. Although all of the porous media used in this study are basically silica, the wetting alteration achieved, as indicated by measurements of spontaneous imbibition, varied considerably.

Wetting conditions in Aerolith

Other than the two-dimensional micromodels, the simplest medium considered here is the synthetic, Aerolith, which contains no clay. A clear distinction was found between more water-wet conditions with high pH aqueous phase and less water-wet with lower pH, in qualitative agreement with flat surface results.

Even Aerolith is not pure silica; it contains about 5% alumina. Table 4-7 shows contact angles measured with A-93 crude oil on several different surfaces. Advancing angles on all these surfaces were high with the pH 4 brine, but lower advancing angles were measured on both glass and sapphire with the pH 8 brine.

surface	pH 4, 0.1 M		pH 8, 0.1 M	
	θ_R	θ_A	θ_R	θ_A
borosilicate glass	50	145	10	20, 90
sapphire ($\alpha\text{-Al}_2\text{O}_3$)	20	150	5	7
hematite (Fe_2O_3)	65, 100	155	55, 155	165

The lower contact angles observed with pH 8 solutions (c.f. also Fig. 4-8) and water-wet conditions in the Aerolith core treated with pH 8 brine are in good agreement. High contact angles with pH 4 do not, however, translate into oil-wet behavior. Water imbibe slowly and oil does not imbibe at all.

If the water advancing contact angle is greater than 133° , oil imbibe into uniformly wetted porous media (Morrow and McCaffery, 1978). Since, on flat glass surfaces, water advancing contact angles were higher than 150° (Fig. 4-8), oil would be expected to imbibe if wetting were altered uniformly. However, porous media contacted with crude oil are not uniformly wetted, but rather develop mixed-wetting. Oil imbibition requires, in addition to a minimum contact angle, that continuous pathways of oil-wet surface be present through the core.

Wetting alteration in Clashach sandstone

Wetting is altered in Clashach sandstone to a greater extent than in Aerolith exposed to the same fluids and aging conditions. Unlike Aerolith, in which the wettability conditions reflected the alteration of contact angles on flat surfaces with brines of varying pH, solution pH appears to exert a secondary effect in the wetting alteration of Clashach sandstone.

Two possible explanations may be suggested. The first is that higher capillary pressures in the less permeable Clashach cores are sufficient to destabilize water films at pH 8 (Hirasaki, 1991). Fig. 4-18 shows two hypothetical disjoining pressure curves representing an oil/brine interface approaching a solid/brine interface with the pH 4 and pH 8 brines.

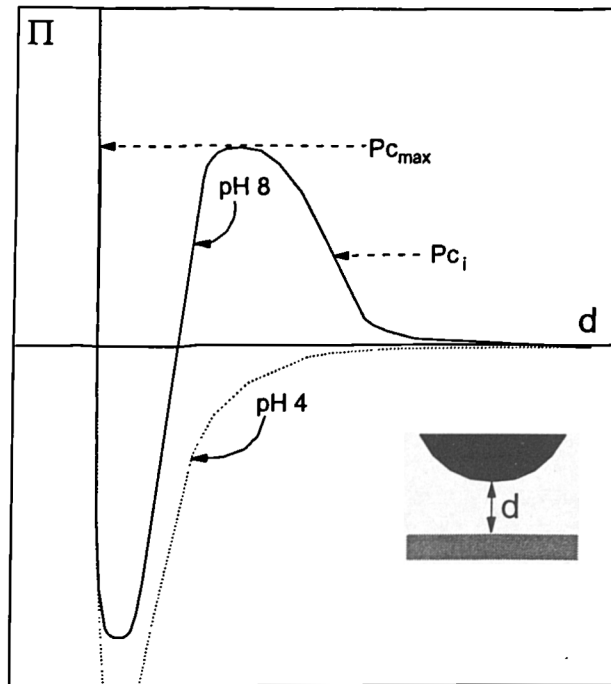


Figure 4-18. Hypothetical disjoining pressure curves for pH 4 and pH 8 brines.

Water films are not stable in the pH 4 case. If P_c exceeds the maximum in the pH 8 disjoining pressure curve, the water film between oil and solid will thin, whereas at lower values of P_c , a water film in the same system is stable. The difference in wetting between pH 4 and pH 8 solutions with A-93 crude oil and a silica surface would be maintained only so long as P_c does not exceed $P_{c_{max}}$.

Capillary pressure differences cannot, however, explain why Clashach became more oil-wet than did Aerolith. To explain that, differences in surface chemistry must be considered. Natural porous media are, of course, made up of many minerals. Although in siliclastic rocks, quartz is usually the dominant mineral, others may be present in significant amounts. Clashach has few clay minerals, but many potassium feldspars which have different surface chemistry than quartz.

In addition, there may be pore coating minerals present in relatively small volumetric amounts, that can have a controlling influence on the surface properties. Clashach, for example, has been reported to have pore coatings of hematite (Fe_2O_3) (Jordan *et al.*, 1994). As shown in Table 4-7, advancing angles between A-93 and either pH 4 or pH 8 brines are greater than 150° on a hematite surface.

Slow Imbibition of Water

In uniformly wetted media, very slow water imbibition would indicate water advancing contact angles close to but less than the 62°, above which neither fluid should imbibe (Morrow and McCaffery, 1978). In mixed-wet conditions, however, bulk water can preserve connected pathways of strongly water-wet surfaces.

Under circumstances where capillary forces are reduced, gravity segregation can play an increased role in production of oil from a core submerged in water, as demonstrated by Schechter *et al.* (1994). Strongly water-wet cores were shown to have imbibition rates that depended on the balance of capillary and gravity forces resulting from addition of varying amounts of surfactant species to alter oil/water IFT. Since

$$P_c = \gamma \left(\frac{1}{r_1} + \frac{1}{r_2} \right) = \gamma \times C$$

where r_1 and r_2 are any two orthogonal radii of curvature, and γ is IFT, P_c can be decreased either by decreasing γ , as Schechter did, or by decreasing the curvature ($C = 1/r_1 + 1/r_2$). The curvature is affected both by pore size and by contact angle. Contact angles that result in flatter interfaces (decreasing curvature) decrease capillary pressure and thus can have an effect analogous to decreasing IFT with respect to the balance between capillary and gravity forces. Visual evidence that may actually document such a transition from a capillary to gravity dominated mechanism in a COBR system has been reported (Zhou *et al.*, 1993), although gravity is usually assumed to be unimportant in short cores.

Adsorption of crude oil components is often assumed to be essentially irreversible, but desorption can also occur (Liu, 1993) as shown in Fig. 3-27. Mennella and Morrow (1994) have also reported slowly decreasing contact angles between A-93 crude oil and brine, measured with a static Wilhelmy plate. One explanation for the very slow uptake of water may be slow desorption of the adsorbed crude oil species. Wetting and contact angle may be changing during long imbibition times. The very long times required to see oil production suggest that the combined effects of a slow surface chemical reaction (desorption) and weak gravity forces, in what might best be called gravity assisted imbibition, are jointly responsible.

Very slow oil production, by whatever mechanism, is likely to be overlooked in laboratory studies, especially in routine tests where times and cores are short. It may well

play an important role in waterflooding at the field scale, however. Imbibition, however slow, is essential to the success of waterfloods in fractured media. Waterfloods in some North Sea chalks, for example, have been more successful than expected, based on laboratory imbibition studies. High gravity forces can be achieved by centrifuging even very short samples, but if desorption is important as well, erroneous conclusions will result because of the time scale of centrifuge experiments.

Optimal Recovery

At what wetting condition is oil recovery maximized? Optimal oil recovery was observed in crude oil-treated Berea sandstone cores with a combined Amott index ($I_{w-o} = I_w - I_o$) of about 0.3, i.e., weakly water-wet cores that imbibed water slowly and did not imbibe oil (Jadhunandan and Morrow, 1995). While subsequent studies have shown similar trends in oil recovery vs. I_w , these studies also were in Berea Sandstones, so the extent to which this relationship is generally applicable is not yet established.

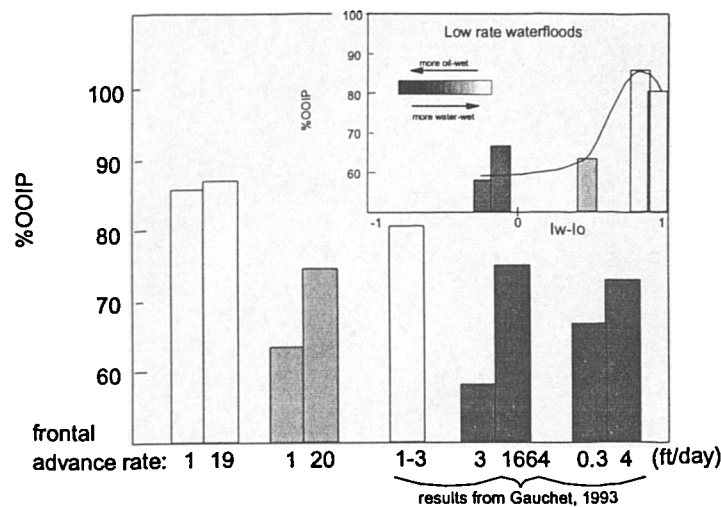


Figure 4-19. Comparisons of displacement efficiencies for waterfloods in Aerolith-10 with varying wettability and flood rate.

In Aerolith treated with a crude oil from France ($I_{w-o} = -0.15$), poorer displacement efficiency was observed than for strongly water-wet cores of the same material saturated with mineral oil ($I_{w-o} = 1$) (Gauchet, 1993). These results are compared with the displacement efficiencies of the present work in Fig. 4-19. Wetting is indicated qualitatively by darker shading for less water-wet conditions, based on imbibition rate and Amott data so that pH 8 can be distinguished from very strongly water-wet conditions.

The less water-wet results vary with flooding rate, whereas the more water-wet recoveries are insensitive to flood rate. Only the lower rate waterfloods (≤ 3 ft/day) are compared in the inset to Fig. 4-19, where they are arranged according to I_{w-o} . Optimal oil recovery efficiency is achieved in the pH 8 waterfloods where imbibition rate is suppressed and I_w is 1.

Clashach displacement efficiencies are less reliably compared because of the differences in initial water saturations. Both cases, pH 4 and pH 8, were nearly neutral on the Amott-Harvey scale, with significant imbibition of both water and oil. The higher apparent efficiency was for pH 8 ($I_{w-o} = 0.15$), on the positive side of the scale, as compared to pH 4 ($I_{w-o} = -0.07$), which is consistent with the results published for Berea, but the magnitude of the difference is exaggerated by the differences in S_{wi} .

Since the relationship between oil recovery efficiency and wettability index goes through a maximum, it is not possible to say *a priori* which of two comparable waterfloods, one more water-wet and the other less water-wet, should be the more efficient without also specifying the maximum and the shape of the curve. Extending the results of Jadhunandan and Morrow (1995) suggests a curve similar to the solid line in Fig. 4-20 for the relationship in Berea. Combining the present results in Aerolith with those of Gauchet (1993), on the other hand, suggests the dotted line for the synthetic porous medium.

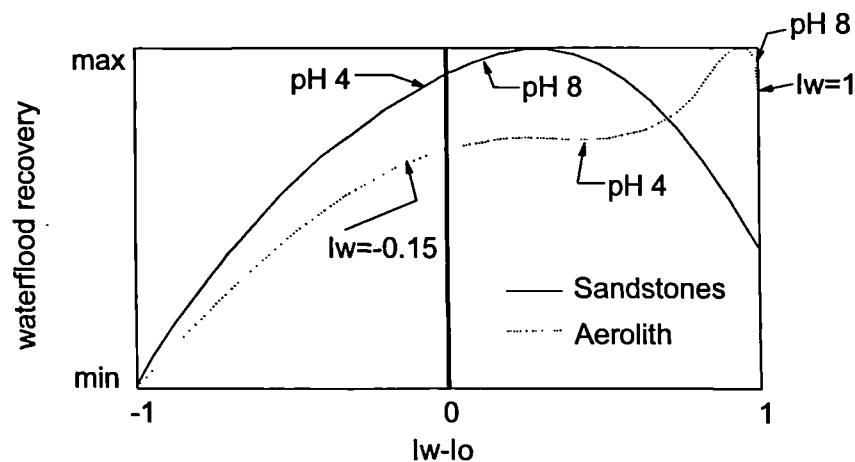


Figure 4-20. Relationships for wettability vs. oil recovery by waterflood may vary for different media.

On the microscopic level, displacement mechanisms are the result of complex interplay between wetting and pore shapes (e.g., Wardlaw, 1982). Depending on the details of the shape and interconnections of the pore space, different displacement mechanisms are observed for similar wetting conditions. For example, trapping of nonwetting phase in a

strongly water-wet medium occurs where there are high aspect ratio pores (i.e. pores with diameters much greater than those of connecting throats). Berea Sandstone is highly trapping medium, whereas Aerolith has much more uniform pores that show less trapping under strongly water-wet conditions, as shown in Fig. 4-21 where spontaneous imbibition curves for Aerolith, Berea, and Clashach under strongly water-wet conditions are compared.

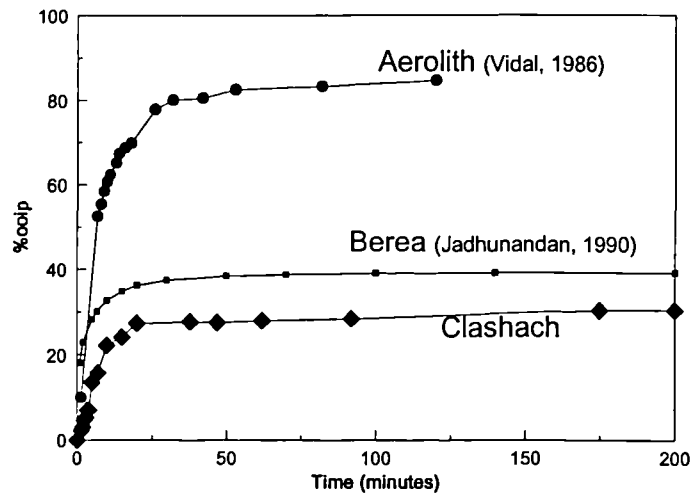


Figure 4-21. Trapping during imbibition into strongly water-wet cores.

Although additional data are needed to complete the picture, it appears that there are different relationships between wetting, as measured by the Amott-Harvey index, and oil displacement efficiency for porous media with significantly different pore structures. These relationships should have in common a maximum in efficiency that lies between strongly water-wet and strongly oil-wet, but the location of the maximum may vary from one rock to another. Many features of actual imbibition experiments, including one or more maxima in the relationship between oil recovery and wetting, are captured in recent network simulations by Dixit *et al.* (1996). The results of these simulations, summarized schematically in Fig. 4-22, show that Amott indices can be used as guides to one of several regimes of wetting.

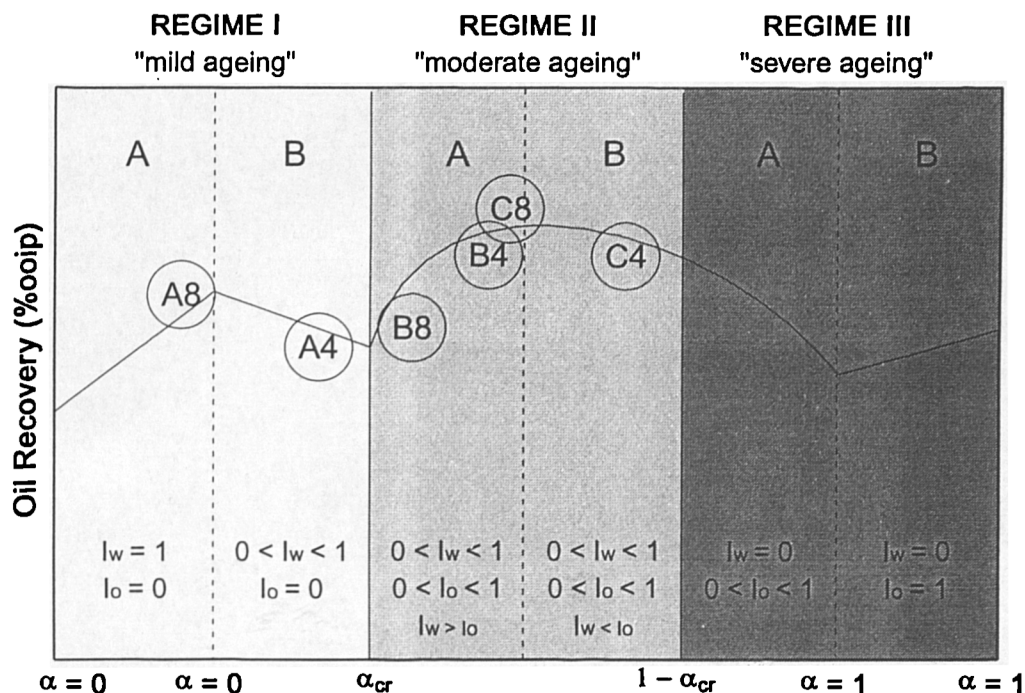


Figure 4-22. Regimes of wetting alteration. The circles suggest relative locations of experimental results (A is Aerolith, B is Berea, and C is Clashach; 4 is pH4, and 8 is pH8 NaCl brine). (after Dixit *et al.*, 1996)

In Regime I, usually corresponding to mild crude oil aging conditions (e.g. high S_{wi} , short time, low temperature), the core remains water-wet. The maximum in oil recovery corresponds to the point where oil-filled pores can have contact angles that range from 0 to 90 degrees and water-wet pathways remain connected throughout the core. Throughout Regime IA, $I_w = 1$, although the rate of water imbibition would be decreasing. The combination of Aerolith, pH8 brine, and A-93 crude oil (indicated by the circled A8) is an example. Beyond the maximum, in Regime IB, oil-filled pores are increasingly oil-wet, but no oil imbibe. Aerolith, treated with pH 4 brine before aging in A-93 crude oil falls in Regime IB. Eventually there are enough oil-filled pores to form a continuous pathway to an outlet. In Regime II, either oil or water can imbibe. All of the Berea and Clashach experiments fall in Regime II. In Regime III, cores are preferentially oil-wet. Both the fraction of non-water-wet surfaces and the contact angles on those altered surfaces are increasing in the simulations that produced the waterflood oil recovery predictions in Fig. 4-22.

Summary

In this chapter, the primary objective has been to investigate how observations of wettability alteration on flat mineral surfaces translate into the behavior observed in porous

media. Oil recovery characteristics were studied by waterflood and spontaneous imbibition experiments in porous media of increasing complexity from glass micromodels, to synthetic core (Aerolith), and outcrop sandstones (Clashach, and Berea). Fluids (A-93 crude oil and 0.1 M NaCl brines) were chosen because they produce very different wetting conditions that depend on pH.

Adsorption of crude oil components in the presence of brine results in development of mixed wetting in glass micromodels and in cores. A variety of mixed-wet displacement mechanism can be demonstrated in glass micromodels where the water advancing contact angles on surfaces with altered wetting can vary from low (but not zero) to very high.

Control of wetting alteration using low ionic strength NaCl solutions of varying pH has been demonstrated in a synthetic, primarily silicate, porous medium (Aerolith-10). A solution which on flat surfaces produces low water advancing contact angles led to more water-wet conditions in a core, whereas less water-wet conditions were produced with a low pH brine for which high water advancing angles were observed. This is the first clear demonstration of the same COBR interactions acting both on flat surfaces and in porous media.

Two outcrop sandstones (Clashach and Berea) also showed more water-wet conditions with the pH 8 than pH 4 brine. Greater change in wetting and less difference between the two pH conditions were found than in experiments with Aerolith. There are several possible explanations. One is that the pore surfaces are not strictly silica. In Clashach, there are coatings of hematite and Berea has clay minerals. Other COBR interactions than those investigated in the smooth surface experiments on glass may well be important. Another reason for somewhat unexpected COBR interactions in the sandstones is that it is difficult to change one variable in isolation. For example, in the Clashach experiments, changing pH affected S_{wi} and, hence, at least two variables (and possibly more) were being examined simultaneously. Another variable may be the brine: we cannot be sure that the brine composition and pH in the sandstones were identical to those of the injected brine. Different mechanisms of COBR interaction will be the subject of Chapter 5.

Oil recovery depends in fairly complex ways on both wetting and pore structure. The Regime theory provides a framework for comparing cores with a wide range of wetting (diagnosed by spontaneous imbibition of water, oil, or both). Conditions in Regimes I and II were produced in this study with a single crude oil by varying brine pH and core types.

Chapter 5

MECHANISMS OF CRUDE OIL INTERACTIONS WITH SOLIDS

There are a number of ways in which crude oils can alter wetting of a solid surface. Depending on surface and interfacial chemistry, the presence (or absence) of water, and ionic composition of the brine phase, one or more of these mechanisms may dominate the crude oil/brine/solid interactions. Drawing on the background provided in the previous four chapters, characteristics of different mechanisms are identified and their likely contributions in conditions of importance to reservoir and laboratory studies are discussed.

Mechanisms by which crude oil components may adsorb on high energy mineral surfaces include nonpolar, polar, acid/base and ion binding interactions. Surface precipitation of asphaltic and other crude oil components 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. An alternative approach is to 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 broad mixtures of compounds in any crude oil, variability of crude oil samples even from the same source, and changes that may occur in a crude oil during storage, all add to the uncertainties of mechanistic studies with crude oils.

Previous chapters have established the framework needed for consideration of the mechanisms of COBR interaction. In Chapter 2, the wettability altering acids and bases that exist in the polar and asphaltene fractions of crude oils were introduced. The influence of oil composition on asphaltene aggregation was reviewed and the use of refractive index as a measure of oil solvent quality was proposed. In Chapter 3, the focus was on oil/brine and oil/brine/solid interactions. A key feature of crude oil/brine interfaces is their amphoteric nature: sites of positive and negative charge can coexist and surface charge density may be high, even near the isoelectric point. Empirical methods that focus on observations of oil and smooth solid in the presence of brine were applied to identify the combinations of crude oil, brine, and solid for which water films are either stable or unstable. Finally, in Chapter 4, a

study of oil and brine in various porous media, showed that the interactions identified on smooth surfaces also controlled wetting in a porous medium of similar material. In sandstone cores, however, wettability changes were less directly predictable from surface measurements. In the course of this work, four major categories of fluid/solid interactions, each with different implications for reservoir wetting, have been observed.

Categories of Crude Oil/Brine/Rock Interactions

The main categories of COBR 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.

Any of these interactions can affect wetting of crude oil/brine/solid ensembles. Each has different kinetics. In addition, temperature can affect more than just the rates at which interactions occur. It is necessary, first to distinguish between these mechanisms, then to identify when each is the dominant factor. Distinctions between mechanisms of interaction are most readily apparent using the smooth surface techniques, already described (Appendix B). After reviewing the evidence for these various mechanisms, the consequences for wetting alteration in sandstone cores will be considered.

Polar interactions

Water advancing contact angles for three crude oils, resulting from oil/solid interactions in the absence of water, were shown in Fig. 2-3. Initially dry surfaces were aged in the crude oils for varying periods of time. After aging, the surfaces were rinsed with toluene and contact angles were measured with decane and distilled water. Polar interactions between crude oil components and the silica surface lead to adsorption that is sufficiently strong that it resists removal by toluene rinsing. In all cases, the advancing angles are intermediate and the extent of interaction, as reflected in the contact angles, changes little with time. Similar results, intermediate values of θ_A that do not change much with aging

time, have been reported for dry glass surfaces aged in solutions of A-93 asphaltenes in toluene (Buckley *et al.*, 1996).

A dry surface, aged in A-93 crude oil for 2 weeks at 80°C, appeared under AFM examination to have patches of adsorbed material (Fig. 3-30). While the AFM evidence is qualitative, it does suggest that the intermediate values of θ_A may be due to partial coverage of the surface by polar interactions in the absence of bulk water. Intermediate θ_A values and substantial hysteresis have been reported on heterogeneous surfaces (Robin and Koci, 1994). Whether only partial coverage is achieved during the adsorption process, or whether toluene washing is responsible for the final appearance and contact angles on these surfaces cannot be distinguished with the available techniques. Direct observation of surfaces by AFM in a liquid cell during the adsorption process might resolve this question and such techniques are becoming available.

Surface precipitation

If the oil is a poor solvent for the asphaltenes, the tendency for wetting alteration is enhanced. This point was illustrated in Chapter 3 in tests of both adhesion (Fig. 3-19) and adsorption (Tables 3-3 and 3-4). Fig. 5-1 shows the effects of removing bulk crude oil, after aging, by either solvents or precipitants. Decane, which causes precipitation from A-

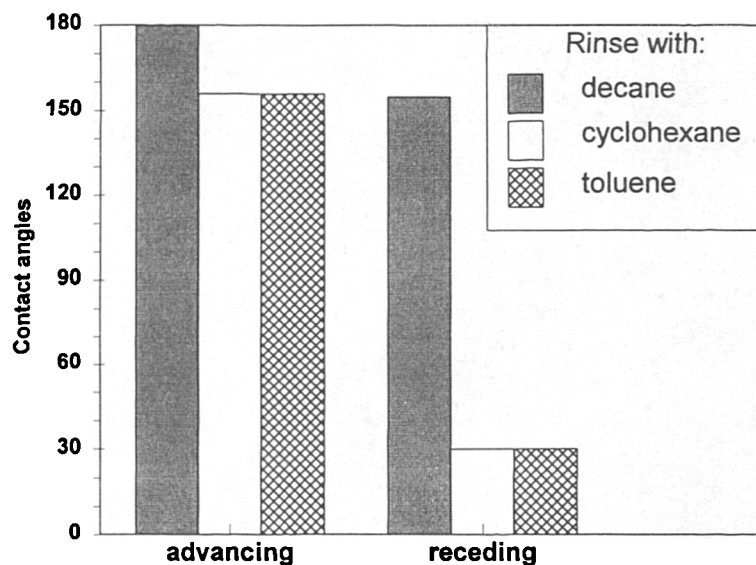


Figure 5-1. If precipitation can occur as the oil is being washed from the surface, both advancing and receding angles are high. Results shown are for glass slides aged in A-93 synthetic reservoir brine, then in A-93 crude oil for 2 weeks at 80°C. Contact angles are measured with a drop of distilled water under decane.

93 crude oil, produces an oil-wet surface. Both advancing and receding angles are high. Washing with either toluene or cyclohexane produces much different results. Gentle washing with these solvents produces a surface with high water advancing angles, low receding angles, and substantial hysteresis between the two. The only difference in treatment between these three surfaces is the changing oil solvent quality as the crude oil is being diluted and

washed away. Once the oil is gone, the surfaces can be submerged and stored indefinitely in decane, without further change.

Fig. 5-2 shows the results of decane/water contact angle measurements on surfaces, all of which were washed with toluene after aging for 2 weeks at 80°C in oil. Solvent quality was varied by addition of isooctane, toluene, or α -methyl-naphthalene, as explained in Chapter 3. The crude oil alone, and its mixture with isooctane, produced the highest advancing angles. The receding angles reveal an important difference, however. In the mixture with isooctane, much higher receding angles are observed as compared to the more typical,

high-hysteresis surface produced by the oil alone. It appears likely that some extent of surface precipitation is superimposed on the other interactions that occur between the oil and a wet surface.

Acid/base interactions

When a separate aqueous phase is present, it plays an important role in mediating oil/solid interactions. The main reason that the water phase is so important is that, 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 this surface charge phenomenon impacts COBR interactions.

Net charge affects water film stability: The influence of DLVO forces in stabilizing a thin film of water between mineral and oil has been explained for bitumen (Takamura and Chow, 1983) and for crude oils (Buckley *et al*, 1989). DLVO forces are most important in

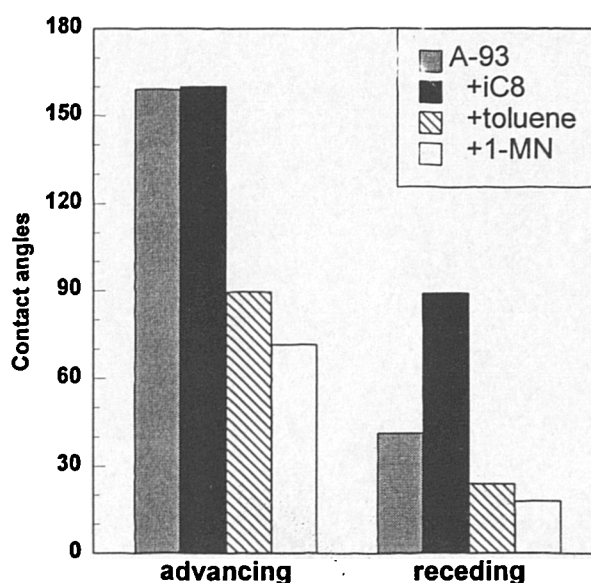
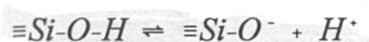


Figure 5-2. Higher receding angle for oil mixed with isooctane may indicate significant surface precipitation. Results shown are for glass slides aged in A-93 synthetic reservoir brine, then in A-93 crude oil for 2 weeks at 80°C, and finally rinsed with toluene. Contact angles are measured with a drop of distilled water under decane.

COBR systems 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. The distribution of ionizable acids and bases at the oil/water interface and their equilibrium constants control surface charge density as a function of brine composition. These available crude oil acidic and basic species can vary widely from one crude oil to another.

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. Net charge is no longer the most important interfacial property. The individual charged species, their distribution and chemistry on both oil and solid surfaces, control both the extent and the strength of bonding of adsorbed crude oil components to mineral surfaces.

Silica surfaces are negatively charged above pH 2 because of the loss of protons from silanol groups:



The species most likely to adsorb are positively charged nitrogen bases (Anderson, 1986). Conversely, calcite surfaces which are positively charged below a pH of about 9.5 (Somasundaran and Agar, 1967) adsorb acidic species (e.g. Morrow *et al.*, 1973; Thomas *et al.*, 1993).

Characteristics of surfaces with wetting altered by acid/base interactions: There is considerable diversity between crude oils in the extent to which they alter wetting by acid/base interactions. A-93 crude oil can produce very high water advancing angles on borosilicate glass surfaces; an example is shown in Fig. 5-3 for a glass surface equilibrated with pH 4, 0.01 M NaCl and aged in oil at 80°C. The initial interaction is fast, as it must be for adhesion to occur (see Fig. 3-19). The contact angle is finite for measurements after only one hour of aging. At this early stage, however, the residual effect of oil after rinsing with toluene is small ($\theta_A = 58^\circ$). After 10 days of aging in this oil, the residual θ_A has increased substantially to 152° and the hysteresis between advancing and receding conditions is dramatic.

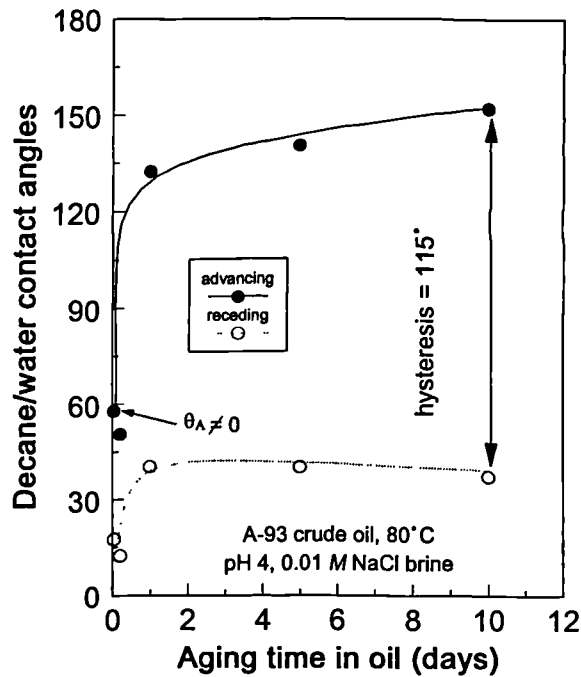


Figure 5-3. Acid/base interactions are the dominant mechanism for wetting alteration on a glass surface soaked in a low pH, low ionic strength NaCl solution before exposure to A-93 crude oil.

Substantial hysteresis is characteristic of these acid/base interactions that can occur on initially water-covered surfaces. The hysteresis can be maintained even if the surface is dried. An adsorbed layer that can be preferentially water-wet or oil-wet, depending on its environment is illustrated in Fig. 5-4. If the adsorbed layer is wetted by the phase most recently in contact with it, whichever phase that is, high values of hysteresis between advancing and receding conditions would result, as shown. In this model, the organic layer **adapts** to whichever is the overlying phase.

A layer of adsorbed water, between the hydrophilic solid and adsorbed layer of oil components is included in the sketches. This water film may be only a few molecular diameters thick or it may swell and even desorb the adsorbed organic material. High water advancing angles that decrease rapidly have been reported for glass surfaces exposed to asphaltene dissolved in toluene (Buckley *et al.*, 1996). Sometimes desorbed material formed rigid films on the water drop that was used in the contact angle measurement. Czarnecka and Gillott (1980) reported little change in the ability for water to swell the interlayers of clays, even though adsorption of asphaltene had made the surfaces hydrophobic.

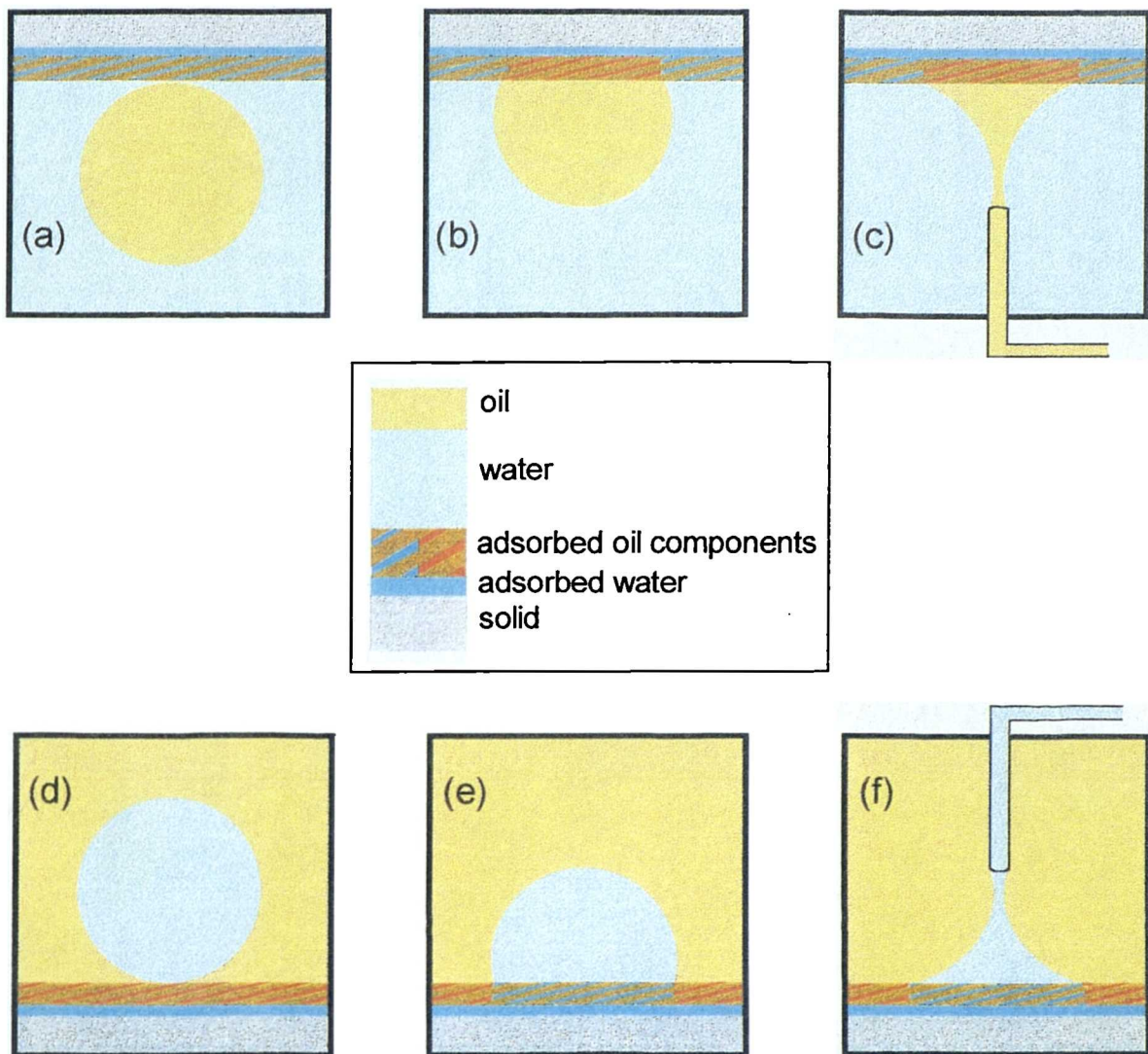


Figure 5-4. Adaptive wetting: The extreme hysteresis observed for some crude oil treated surfaces can be explained if the adsorbed layer equilibrates with and is wetted by whichever phase it is contacting. (a)-(c) illustrate an oil drop on the adsorbed layer initially in contact with water. The inverse case, a water drop brought into contact with an oil covered surface, is shown in (d)-(f). Initially the adsorbed layer is nonwetting to the drop phase (a and d). As a drop sits on the surface, the area beneath it equilibrates with the drop phase (b and e), so that the drop is wetting when it is withdrawn (c and f).

The complex effects of aging temperature on acid/base interactions are illustrated in Fig. 5-5. Sulimar Queen crude oil alters wetting of glass surfaces less than A-93 does. Polar interactions on dry surfaces are little affected by either aging time or temperature, as observed for other crude oils (Fig.2-3). The acid/base interactions depend on both the time and temperature of aging. For six hours of aging in oil at 25°C, only pH 4-treated surfaces have finite water advancing angles. All other surfaces remain strongly water-wet. Much greater changes have occurred on surfaces aged at 80°C during a similar six hour period. The effect of pH again is evident in the higher contact angles for pH 4-treated surfaces. The comparisons between 25°C and 80°C are quite a bit different after 20 days of aging. The advancing angles on surfaces treated at lower temperature are reasonably similar to those aged at high temperature, and sometimes the low temperature surface is the less water-wet of the two. The main difference appears to be the rate of change. At 80°C contact angles change quickly whereas at 25°C longer periods are required to reach stable values of θ_A .

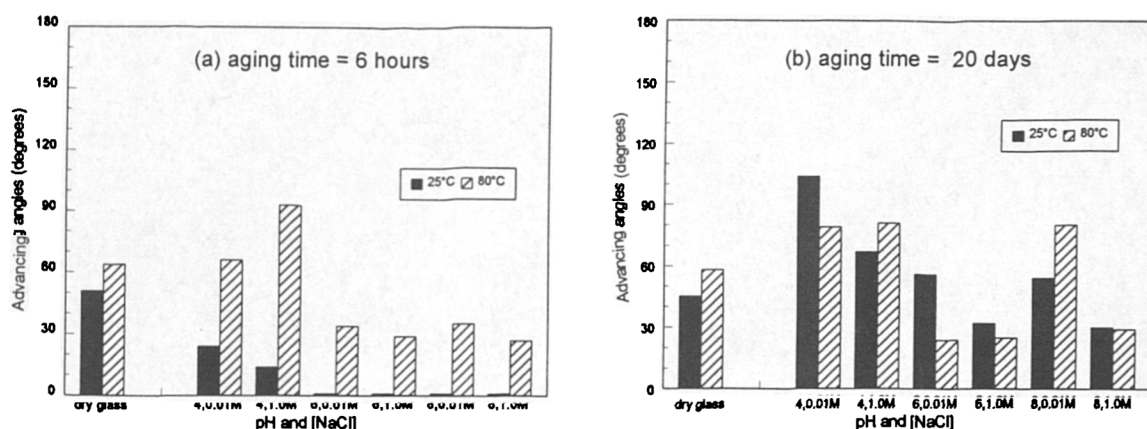


Figure 5-5. The effects of aging temperature on polar and acid/base interactions between Sulimar Queen crude oil and glass surfaces are shown by contact angles measured with decane and distilled water. (after Wu, 1996)

Ion binding

One of the major problems encountered in attempts to relate oil composition to wetting alteration in cores is that the simple relationships of acids adsorbing on calcite and bases adsorbing on silica seem not to apply to carbonate and sandstone rocks (Denekas *et al.*, 1959; Cuiec, 1975). There are several reasons why this may be so, one of which is that di-

and multi-valent ions can bind at either the solid/water or oil/water interfaces and can bridge between the two. In this mechanism of wetting alteration, ions of the same sign as the solid surface are the adsorbing species. The details are undoubtedly complex. Ions may bind selectively at the oil/water and solid/water interfaces in preference to bridging between them, favoring repulsion instead of enhancing attractive interactions.

When present, Ca^{2+} ions mask the purely acid/base interactions. 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, with high contact angles between decane and water as shown in Fig. 5-6, but the interactions are very dependent on temperature. High hysteresis, similar to that observed for acid/base interactions, is shown in

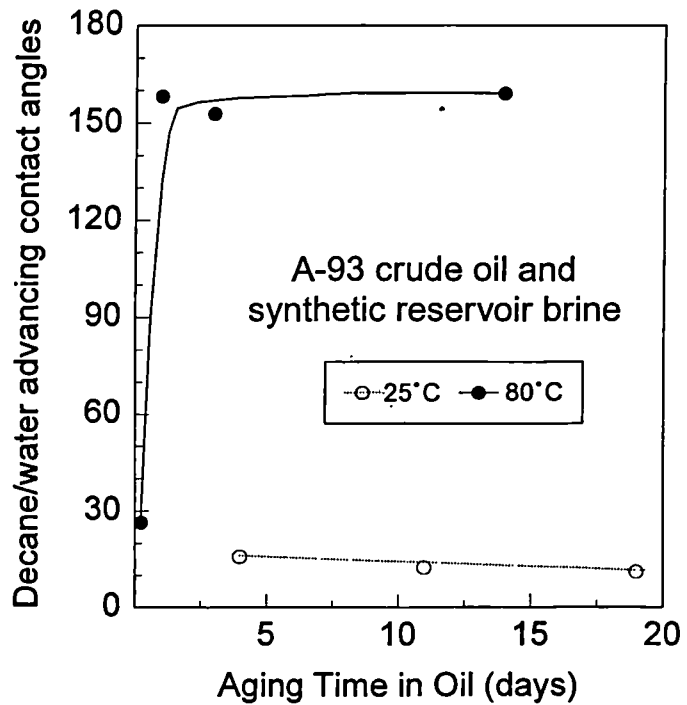


Figure 5-6. Ion binding interactions occur when there are higher valency ions in the brine. Binding at either the oil or solid interfaces can reduce interaction; bridging between them increases wetting alteration.

Figs. 5-1 (toluene and cyclohexane rinsing) and 5-2. Interactions via ion-binding appear to be much more resistant to desorption than acid/base interactions (see Fig. 3-27).

Summary of COBR interactions

A summary of the interactions identified and some of their relevant characteristics is assembled in Table 5-1. The graphical notation used in column 5, summarizing the rate and extent of surface alteration for different conditions of pH, temperature, etc., is illustrated in Fig. 5-7.

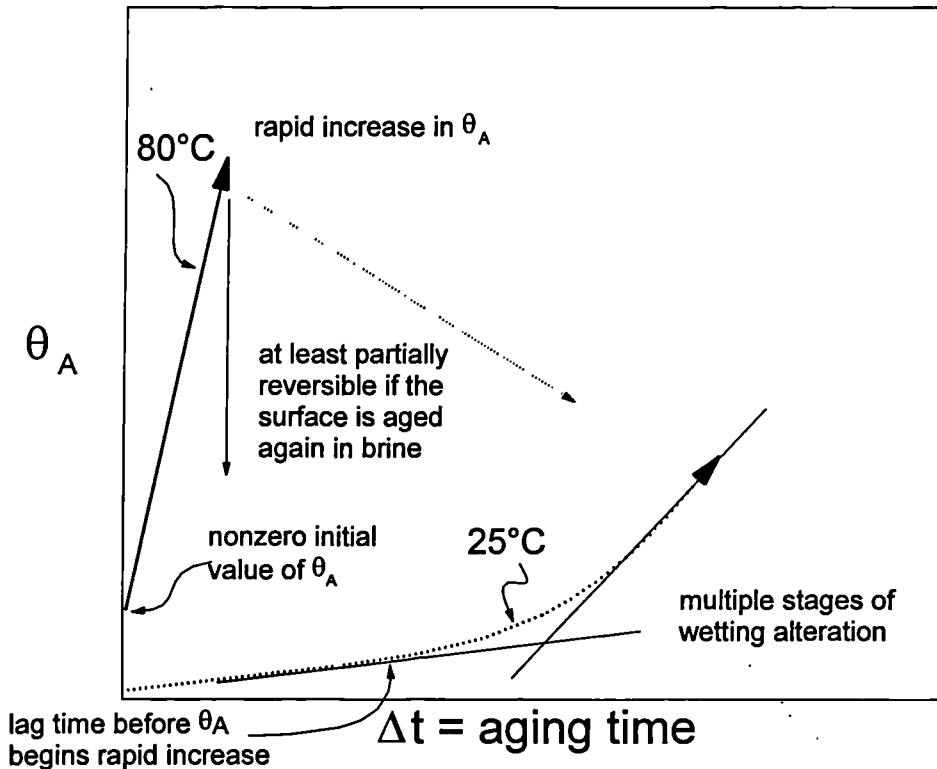
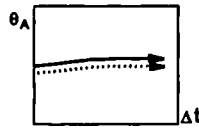
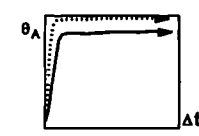
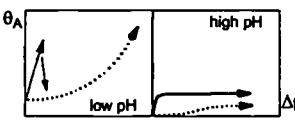
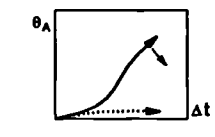


Figure 5-7. Illustrations of some of the changes in θ_A that typify different conditions of interaction. Variables include aging time, aging temperature, and initial θ_A (based on adhesion results). Reversibility, by aging in brine, is indicated by the downward arrows.

This is by no means an exhaustive list. Other mechanisms are possible and, in specific circumstances, may well dominate oil/solid interactions. For example, one mechanism that could dominate over those listed in Table 5-1 is chemisorption of carboxylic acids on hematite. Adsorption of oleic acid adsorbs near the zero point of charge of a hematite surface is stronger than the physisorption of negatively charged acid and positively charged surface at low pH (Peck *et al.*, 1966).

Table 5-1. Mechanisms of interaction between crude oils, brine, and solid surfaces. (Graphical notation is explained in Fig. 5-7)				
Type	Description	θ_A	hysteresis ($\theta_A - \theta_R$)	Effects of aging conditions (time, temperature, reversibility)
Polar	If there is no water initially present, the strongest interactions are between polar atoms (N,S,O) and polar surface sites. These may not be as strong as interactions that can occur in the presence of an aqueous phase. (see Fig. 2-3)	$\sim 90^\circ$	moderate	
Surface precipitation	Occurs when oil is a poor solvent for its asphaltenes. Changes in T, P, and in oil composition affect solvent properties. (see Figs. 5-1, 5-2)	$\sim 180^\circ$	low	
Acid/base	Coulombic interactions between ionized acidic and basic sites. If surface is negative (e.g. silica), positively charged basic nitrogen can adsorb. In experiments with NaCl or other monovalent salt solutions at low concentration, solution pH dominates the extent of interactions between a given oil and mineral surface. (Figs. 5-3, 5-5)	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. In a reservoir, both acid/base and ion binding mechanisms would be likely, depending on mineral surfaces and brine. (see Figs. 5-1, 5-2, 5-6)	depends on oil & brine	high	

Crude Oil Properties that Impact COBR Wetting

Acid and base numbers

How a particular crude oil interacts with mineral surfaces must be a function of its composition although a clear relationship between commonly measured crude oil properties and wetting alteration has never been shown. In part, this is undoubtedly due to the multiple ways that crude oils can interact with solids. Having identified some of these mechanisms, it is worthwhile to reexamine crude oil composition and begin to identify trends in their tendencies to alter wetting.

Figs. 5-8 shows acid and base numbers for selected crude oils. (Additional acid and base number data are given in Appendix A.) In Fig. 5-8a, the oils are ranked in order from the highest to lowest acid number. A similar ranking, using base number, is shown in Fig. 5-8b. A-93 has the highest base number of any of the oils in this group; Moutray is the most acidic.

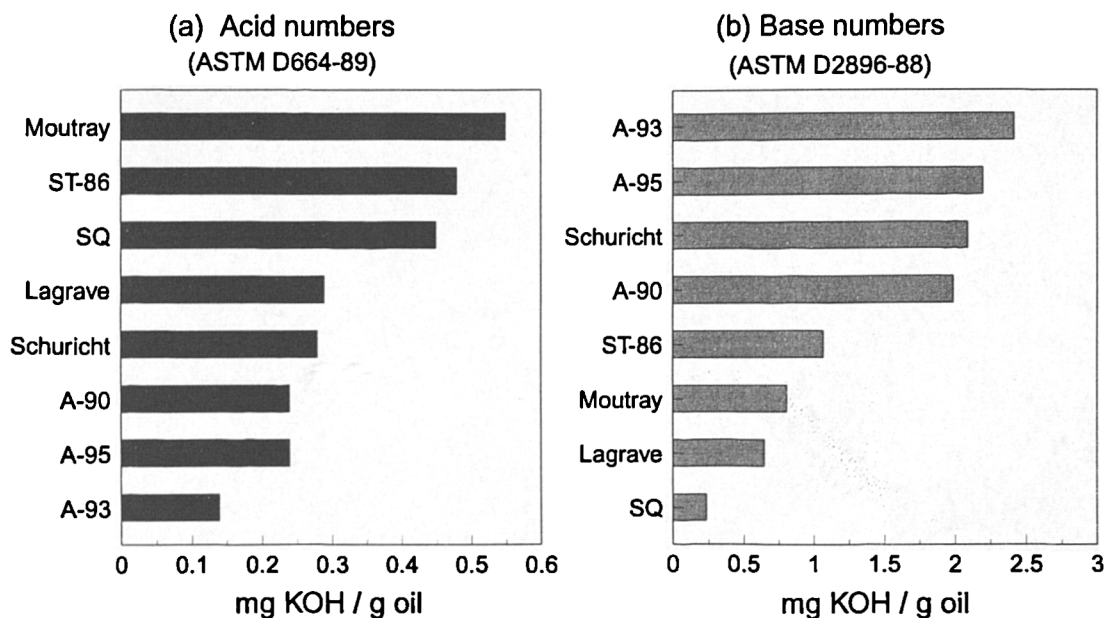


Figure 5-8. Acid and base numbers of selected crude oils.

Solvent quality

Another important factor is the solvent quality of the oil with respect to its asphaltenes. Asphaltene aggregates vary in size with solvent quality (Chapter 2) and the balance between interaction mechanisms—ionic adsorption and surface precipitation—shifts as solvent quality changes with temperature, pressure, and oil composition. Comparing wetting alteration for an oil that is a good solvent with one that is marginal is the source of some confusion since the interaction mechanisms differ significantly. Table 5-2 lists estimates of the refractive index of several crude oil samples and the refractive index at which precipitation is first observed (P_{RI}) with n-heptane added as precipitant. API gravity (inversely related to density) is another indicator of solvent quality and is included in Table 5-2.

Table 5-2. Refractive indices of selected crude oils.			
Crude oil	°API	n_D^{20}	P_{RI} (n-heptane)
A-93	25.5	1.520	1.446
Lagrove	41.3	1.470	1.453
Moutray	35.2	1.483	1.432
Schuricht	24.6	1.513	1.448
ST-87	27.8	1.496	no ppt.

The Lagrove sample is a poor solvent for its asphaltenes (high API gravity and low RI); A-93 and Schuricht are the best solvents in this group of crude oils. ST-87 is the only one of this group that has no n-heptane asphaltenes. Fig. 5-9 ranks selected oils according to their API gravities.

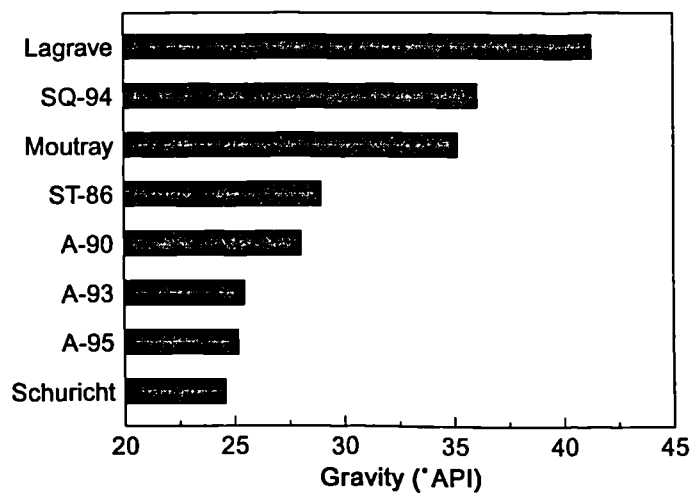


Figure 5-9. API gravity at 60°F for selected crude oils.

Consequences of Fluid/Solid Interactions in Sandstone Cores

It is likely that more than one mechanism of interaction contributes to COBR interactions. Nevertheless, by comparing the most acidic and most basic oils, and oils of varying solvent quality, it is possible to see differences in wetting alteration that are consistent with the proposed mechanisms.

Surface precipitation

The best known example of wettability alteration by destabilizing the asphaltenes in a crude oil is the work of Salathiel with oil from the East Texas field (1973). In order to induce wettability alteration in cores, the crude oil was diluted with n-heptane. Surface precipitation is the most likely mechanism responsible for the development of mixed-wet conditions in this case.

Lagrange crude oil readily alters wetting on silica and in sandstone cores (Morrow *et al.*, 1994), despite having only an intermediate acid number and low base number. Significant production problems were encountered in development of the Lagrange oilfield that were identified as mainly due to deposition of asphaltenes (Garland, 1989). The laboratory sample is a very poor asphaltene solvent.

Acid/base interactions

An example of wetting alteration in cores by acid/base interactions was presented in Chapter 4. The effect of aging Aerolith-10, a synthetic porous medium that is mainly silica, in A-93 crude oil was shown to vary depending on brine pH. Low pH, favoring positive charge of basic functional groups, produced weakly water-wet conditions ($I_w = 0.5$), whereas at higher pH with the same crude oil and aging conditions strongly water-wet conditions ($I_w = 1$) were maintained. Interactions in natural sandstones were more complex. That is not to say that acid/base interactions are unimportant in natural porous media, but rather that they cannot as readily be isolated from other contributing factors.

Ion binding

Wetting alteration with Moutray is particularly sensitive to the concentration of divalent calcium ions in the brine phase. Fig. 5-10 shows a comparison of imbibition rates for cores aged with five different mixtures of NaCl and CaCl₂ followed by aging in Moutray crude oil at room temperature (Jadhunandan, 1990). To facilitate comparisons, the time scale has been converted to dimensionless form using the correlation of Zhang *et al.* (1995) as defined in Chapter 4. The very strongly water-wet correlation is also included for comparison.

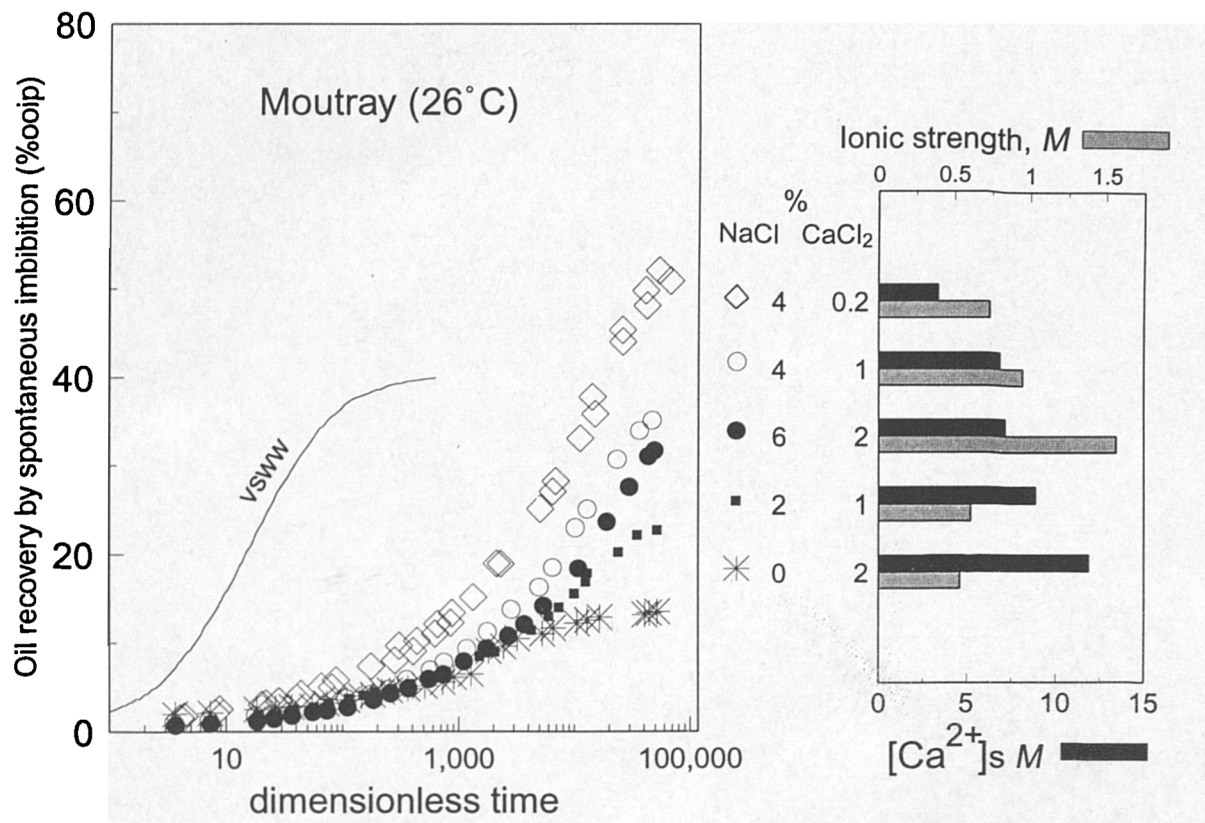


Figure 5-10. Imbibition rate for Berea sandstone cores aged at 26°C in Moutray crude oil is very sensitive to the concentration of calcium ions, especially the concentration in the double layer near the charged surface (as shown in the bar graph). (data from Jadhunandan, 1990)

In Table 5-3, a selection of brine mixtures is listed in order of increasing ionic strength. The concentration of Ca²⁺ ions in these mixtures at a negatively charged surface (-0.2 C/m²) has been calculated from the Grahame equation (Israelachvili, 1991). As the bar graph to the right of the legend in Fig. 5-10 illustrates, the rate of imbibition decreases with increasing surface concentration of Ca²⁺.

Table 5-3. Ionic strength and surface concentration of divalent calcium ion in brines of varying composition.					
NaCl		CaCl ₂		I	[Ca ²⁺] _s
wt %	M	wt %	M	M	M
	0	2	0.18	0.54	11.9
2	0.34	1	0.09	0.61	8.9
4	0.68	0.2	0.02	0.74	3.4
4	0.68	0.5	0.05	0.82	5.4
4	0.68	1	0.09	0.95	6.9
6	1.03	0.2	0.02	1.08	2.3
4	0.68	2	0.18	1.22	8.5
6	1.03	2	0.18	1.57	7.2
A-93 synthetic reservoir brine				0.38	
sea water				0.68	
Sulimar Queen synthetic brine				5.84	

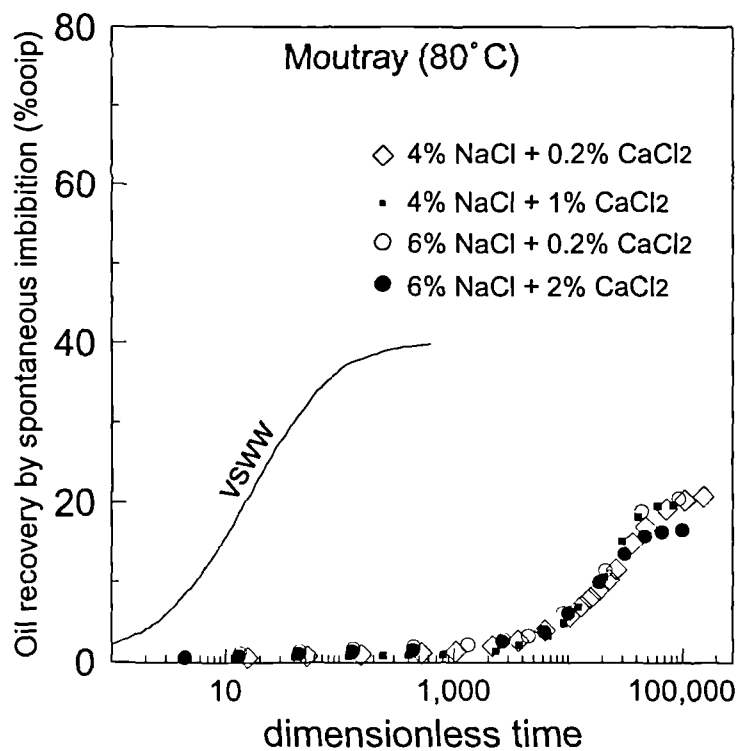


Figure 5-11. Imbibition rate for Berea sandstone cores aged at 80°C in Moutray crude oil is much less sensitive to brine composition. (data from Jadhunandan, 1990)

Differences in imbibition rates for cores treated with different brines are much less significant after aging for 10 days at 80°C (Fig. 5-11), suggesting that the wettability conditions in the cores for which water imbibition rates are shown in Fig. 5-10 have not reached equilibrium after 10 days of aging at room temperature. Slow rates of interaction are one of the characteristics of the ion binding mechanism (Table 5-1). The calcium ion effect on the rate at which equilibrium is approached at room temperature is strong evidence for the participation of Ca^{2+} in the mechanism by which Moutray alters the wetting of Berea sandstone. The ion binding mechanism provides a means for negatively charged carboxylic acids to alter the wetting of negatively charged mineral surfaces and is likely to be the dominant mechanism for acidic oils with sandstones.

Evaluating wetting alteration potential of different crude oils

Each crude oil is different. No one measurement can provide a basis of comparison of the potential for wetting alteration for all oils. The different effects of calcium ion with different crude oils are illustrated by comparing Moutray (Fig. 5-10) with A-92 (Fig. 5-12) and ST-86 crude oil (Fig. 5-13). In the latter two cases, increasing $[\text{Ca}^{2+}]_s$ does not suppress the rate of imbibition either at 25° or 80°C. With A-92, the 2% CaCl_2 brine results actually appear to be slightly more water-wet, whereas brine composition has very little effect on cores aged in ST-86. In both cases, imbibition rate is suppressed by increasing the aging temperature.

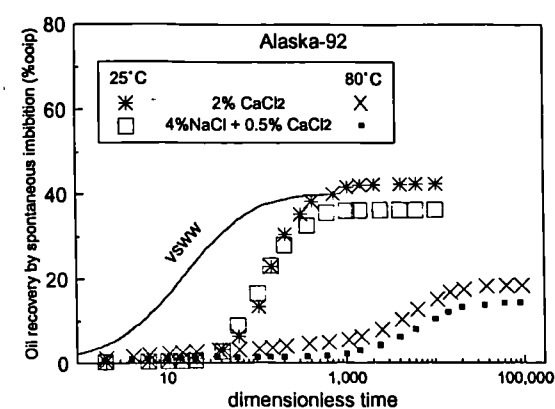


Figure 5-12. Imbibition rate for Berea sandstone cores aged in Alaska-92 crude oil. Dependence on calcium ion concentration is reversed from that observed for Moutray. (data from Yildiz, 1996)

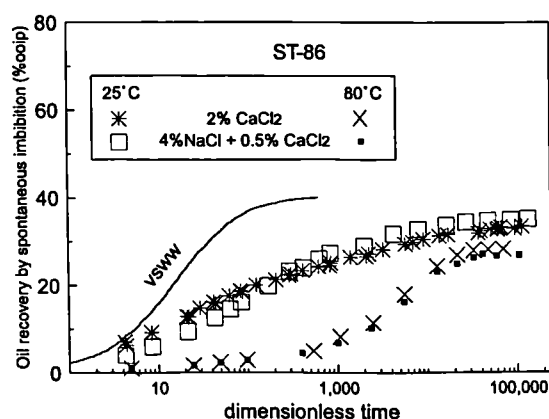


Figure 5-13. Imbibition rate for Berea sandstone cores aged in ST-86 crude oil. There is little or no dependence on calcium ion concentration. (data from Jadhunandan, 1990)

The acid numbers for various oils can help to explain why calcium ions are more important with one than another. The Prudhoe Bay oil samples have far more basic than acidic functional groups. Acid/base interactions between A-92's positively charged nitrogen bases and the mineral surface are likely a significant mechanism of wettability alteration. CaCl_2 concentration contributes to the overall ionic strength of the brine, but has much less influence in terms of specific adsorption interactions than it did in the case of Moutray.

ST-86 has comparable acid and base numbers and neither is particularly high. Fits to zeta potential measurements (discussed in Chapter 3) showed almost the same number of acidic and basic sites at the oil/brine interface. Interactions with the surface are relatively weak, regardless of brine composition, for this oil. Cores aged at 80°C for 10 days imbibe water more slowly than those aged at room temperature, but the amount of water imbibed is reduced only slightly (Fig. 5-13).

The extent of wetting alteration with any oil can vary over a considerable range, depending on the type of rock and conditions of aging. Amott water imbibition tests at reasonably comparable conditions are summarized in Table 5-4 for six different oils all tested in Berea sandstone. Each of these tests is but one of many with the six crude oils. The selected data are for those approaching equilibrium conditions ($T_a = 80\text{-}88^\circ\text{C}$, $t_a = 10$ to 15 days). The brines vary, but none are low in ionic strength and all have some calcium. S_{wi} varies from a low of 24 to a high of 29%. Starting with the least water-wet, we can make the following observations:

- Moutray has the highest acid number of the oils in Table 5-4. Ion-binding is an important mechanism of interaction (Fig. 5-10).
- Lagrave has the highest API gravity and is the poorest solvent for its asphaltenes. Surface precipitation causes wetting alteration.
- A-93 has the highest base number of the oils tested so far. It can participate in acid/base interactions between negatively charged mineral surfaces via positively charged basic components.
- Sulimar Queen has the lowest base number and a significant number of acidic groups. Its API gravity is comparable to Moutray and second only to Lagrave. Thus both ion-binding and surface precipitation may contribute to wetting alteration.
- Schuricht has a high base number. The effect of acid/base interactions for this oil may be partially countered by two factors.

- (1) lowest API gravity and thus one of the best asphaltene solvent of these oils, and
 - (2) relatively high S_{wi} during the aging period.
- ST-86 changed wetting least of this group of oils. It is a good solvent with a low API gravity. It has intermediate numbers of both acids and bases. Electrophoresis showed that there were approximately equal numbers of these at the oil/water interface.

Crude oil	°API	(mg KOH/g oil)		Aging Conditions				Amott Indices	
		Acid #	Base #	brine	S_{wi} (%)	Ta (°C)	ta (days)	I_w	I_o
A-93 ¹	26	0.14	2.42	A-93 synthetic reservoir brine	25	88	10	0.45	—
Lagrange ¹	41	0.29	0.65	2% CaCl ₂	25	80	14	0.32	—
Moutray ²	35	0.55	0.81	4% NaCl 0.5% CaCl ₂	24	80	10	0.32	0.03
Schuricht ³	25	0.28	2.09	2.5% NaCl 0.5% CaCl ₂	29	80	15	0.52	—
ST-86 ²	28	0.48	1.07	4% NaCl 0.5% CaCl ₂	25	80	10	0.60	0.00
Sulimar Queen	36	0.45	0.24	3/4 SQ reservoir brine	29	80	14	0.48	0.00

¹ Morrow *et al.*, 1994; ² Jadhunandan, 1990; ³ Villard *et al.*, 1993

Fig. 5-14 shows I_w for each of the COBR ensembles in Table 5-4. The oils fall into three groups: lower (25-28 °API), intermediate (35-36 °API), and higher (41 °API) gravity oils. These are colored darker to lighter in Fig. 5-14 to emphasize that the lower gravity oils are better solvents for asphaltenes. Above each bar is a number corresponding to the ratio of base to acid numbers.

There are two trends apparent in this set of data.

1. cores are less water-wet as API gravity increases, and
2. cores exposed to oils of similar gravity are less water-wet as the ratio of bases to acids increases.

Multiple mechanisms of interaction help to explain why ST-86 and Lagrange—with the same ratios of base to acid numbers—have such different effects on wetting.

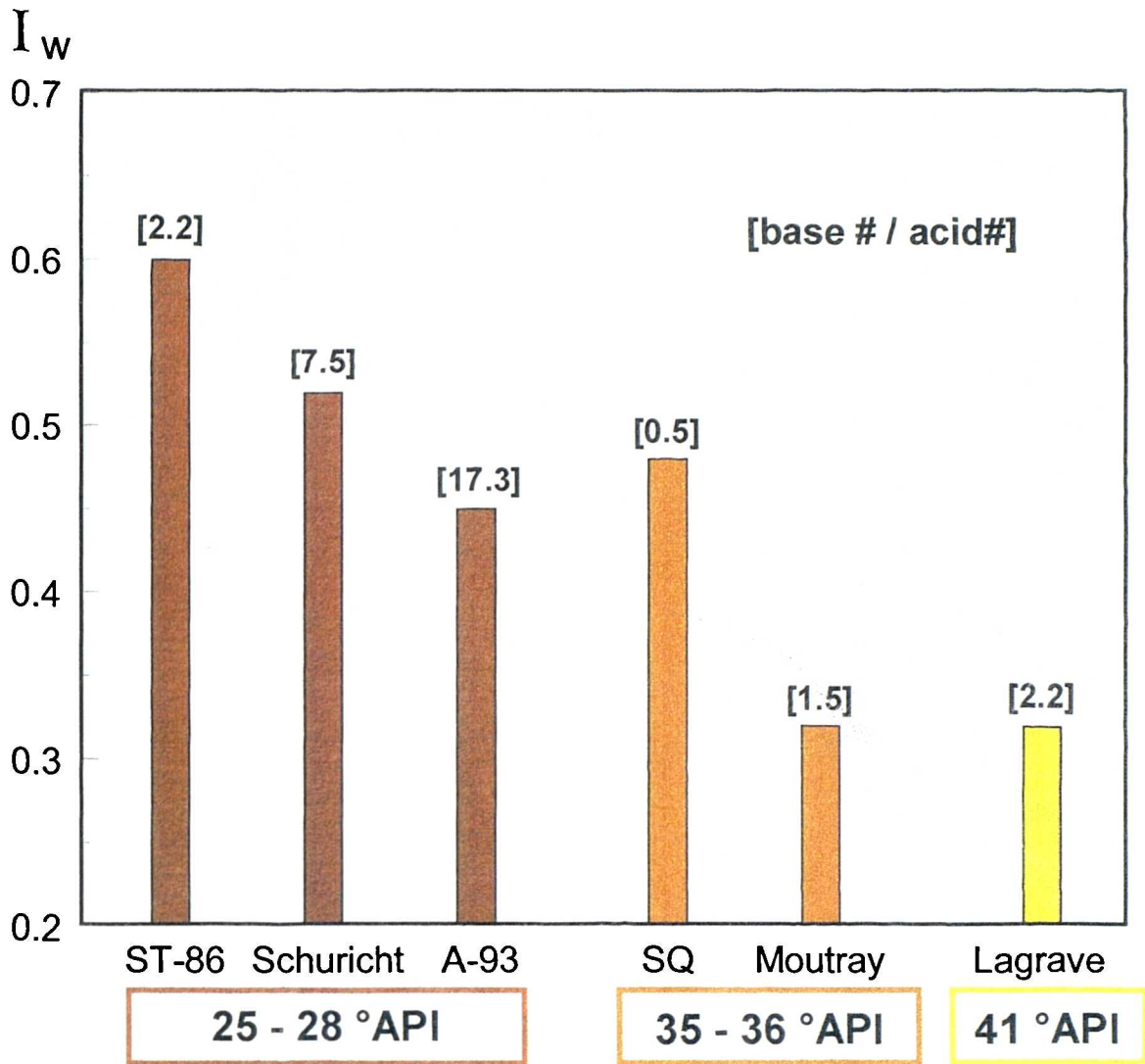


Figure 5-14. The effects of different crude oils on the wettability of Berea sandstone cores can best be compared by grouping the oils according to their solvent quality (estimated here by API gravity), then comparing acidic and basic contributions. Experimental details and references for the I_w data are in Table 5-4.

Summary

There are multiple mechanisms by which crude oil components can adsorb on mineral surfaces and alter the wetting tendencies of reservoir rocks. Four modes of interaction that have been identified in this chapter are polar, surface precipitation, acid/base, and ion binding interactions. These mechanisms have been demonstrated for a range of different oils and porous media. The extent to which any one mechanism may dominate the COBR interactions for a specific suite of oil, brine, and rock can be explained by consideration of the acidic, basic, and solvent properties of the crude oil, the brine composition, and rock surface mineralogy.

Some suggestions for testing of crude oils with regard to their potential to alter reservoir wettability have evolved from the results of the mechanistic studies of wetting alteration presented in this dissertation. In this final chapter, these suggestions, together with a summary of the main contributions of this dissertation, and recommendations for future directions in wettability research are presented.

Suggestions for COBR Wettability Testing

While the interactions between a specific oil and rock are sufficiently complicated that exceptions to any trend will always be found, some general recommendations can now be made for assessing the extent to which a specific crude oil is likely to alter wetting. The properties of interest can be divided into tests of (1) chemical properties, (2) fluid/fluid interfacial effects, and (3) measurements that focus directly on the fluid/solid COBR interactions.

Chemical and physical properties of the crude oil—the G-AB profile

For each crude oil, a profile that quantifies its acid, base, and solvent properties is needed. In its simplest form, this would include gravity, acid number, and base number, an oil's G-AB profile.

Beyond this simple characterization, more detailed information is needed, including refractive indices and elemental analyses for the oil. ASTM standard asphaltene precipitation determines the amount of asphaltene. Cloud point measurements identify the onset of wax precipitation. P_{RI} provides an estimate of asphaltene stability.

Crude oil/brine interfacial properties

The interfacially active components of a crude oil adsorb on mineral surfaces to alter wetting. Thus it is important to understand the interfacial properties of crude oils. The change in IFT with pH of the brine phase provides clues about the acids and bases at the crude oil/brine interface. Additional evidence—from the zeta potentials of emulsified oil droplets—is valuable in completing the picture of ionized interfacial species that are available for adsorption on a mineral surface.

COBR interactions

While the chemical, physical, and interfacial properties of a crude are all factors in the extent to which wetting can be altered by a crude oil, the full suite of variables must include the solids and their geometric arrangement to form the surfaces of pores in reservoir rocks. The history of fluid occupancy of the pore space is important as well.

Tests of adsorption of crude oil components in the presence of brine on representative surfaces can demonstrate the interactions by which wetting is altered. Whether silica is adequately representative of sandstones or calcite of limestones and dolomites is an open question.

In cores, wetting is best characterized by one of the various tests that measure spontaneous imbibition of water and of oil. Indirect measures—the shapes of relative permeability curves or end-point saturations, for example—can be misleading with respect to wetting. Also misleading can be studies of crude oil fractions or experiments that do not include the brine phase.

The effects of temperature and pressure are complex. While it has suited the purpose of this thesis to report work at ambient conditions as well as at elevated temperatures, there is no direct way to scale room temperature results to reservoir conditions. If the purpose of a study is to establish the wetting of a particular reservoir, reservoir conditions of temperature, pressure, and oil composition cannot be avoided.

Summary of the Main Contributions of this Work

The work described in this thesis was aimed toward understanding how crude oils alter reservoir wetting and the effect of wetting alteration on oil recovery. Primary emphasis has been on the first question: how do crude oils alter the wetting of reservoir rocks? An important contribution of this work has been to identify the full suite of variables that must be considered and to demonstrate how they affect crude oil/brine/rock interactions.

Polar components in the crude oil have long been suspected of participating in adsorption and wetting alteration. In this work we have shown that the interactions of those polar components depend in part on the solvent environment in the crude oil. We have developed a simple way to quantify the ability of the oil to act as a solvent for its asphaltenes, using refractive index as a measure of solvent quality. Surface precipitation from oils that

Other mechanisms depend directly on the interfacial properties of the polar oil components. In the presence of water, organic acids and bases both can ionize, resulting in an interface that is zwitterionic. Interfacial tension has been shown to be highest over the range of brine conditions where both positive and negative sites are ionized; IFT decreases when only acids or bases, but not both, are charged. A novel explanation of crude oil adhesion that depends on both the zwitterionic character of the interface and the tendency of asphaltenes to aggregate in oils of poor solvent quality has been proposed.

The acidic and basic oil components can interact directly with acidic or basic surfaces. Wetting alteration has been demonstrated using a basic crude oil in a synthetic core of silicate (acidic) material where pH controls the extent of wetting alteration in the core, just as it does on smooth surfaces. This result establishes an important link between contact angles measured for crude oil/brine/solid systems and imbibition measurements of wetting alteration in cores exposed to crude oil.

Identification of multiple mechanisms by which crude oils and rocks interact is a key contribution of this work. We have shown specific instances where interactions of oils with Berea sandstone cores can vary depending on the acidity, basicity, and solvent quality of the oil. A simple profile composed of the gravity, acid, and base numbers (the G-AB profile) is proposed for evaluating the potential of crude oils to alter wetting.

Future Directions for Wettability Research

Work on the mechanisms by which crude oils affect reservoir wetting have made clear that temperature can affect not only the rate, but the balance between various competing interactions. Thus it is difficult to predict the outcome of COBR interactions at high temperature from studies at low temperature. Compositional effects also play a role. Systematic wettability studies at high temperatures and pressures are needed.

One of the results of this study is the conclusion that sandstones are not well represented by glass surfaces. Tests of some of the other components of sandstones—micas, feldspars, clays and other pore-coating materials—are needed to establish more predictive surface tests for wetting alteration. The important area of carbonate rocks has not been addressed and should be the focus of future studies.

The work reported here has established that there are a number of different mechanisms by which wetting alteration can occur. Better understanding of these and other mechanisms of interaction require studies with well-characterized compounds. To be useful

as models, compounds would need to have very high molecular weights and a small fraction of acidic and/or basic functionality.

Translating an improved understanding of where and how much wetting is altered in an oil reservoir into improved prediction of the outcome of waterfloods and other improved recovery techniques is another important step. Improved understanding of the displacement mechanisms in mixed-wet systems, and the ways in which these mechanisms can vary with rate are needed.

Beyond understanding what reservoir wetting is, lies the possibility of exercising some control over wetting. Wettability control on a limited scale would apply to the area immediately around a well-bore to improve injectivity or oil productivity. Undoubtedly wettability changes already occur with various well treatments. Understanding and optimizing these changes would be a step forward. Choice of waterflood injection brine composition, temperature of injected fluids, and control over reservoir pressure are more global factors which can potentially affect wetting over much larger portions of the reservoir. These wettability changes may already be occurring during production. The objective of future research should be to understand the wettability consequences and to manage the reservoir, with respect to wettability, in a way that optimizes oil recovery.

Concluding Remarks

Wetting of oil reservoirs can only be understood when all of the relevant mechanisms of interaction between crude oil components and the surfaces with which they come into contact are considered. The problem cannot be simplified by contacting oil directly with solid under anhydrous conditions. Neither can fractions of the oil be readily substituted for the whole oil mixture. The central thesis of this study is that the interactions between crude oils, brines, and rocks are affected by the presence and compositions of all three phases. Factors which have been studied in some detail include the effects of oil composition, brine composition, and temperature. Other important factors are recognized which deserve additional attention. Of these, two of the most important may well be (1) the interactions of oil and brine with different mineral surfaces, and (2) interactions at more realistic conditions of temperature, pressure, and oil composition. Studies are proceeding in both of these important areas.

Appendix A

CRUDE OILS AND BRINES—FLUID PROPERTIES

Chemical, physical, and interfacial properties measured for various brines and crude oils used in this study are gathered in this appendix for reference.

Crude Oil Samples

During the course of our wettability studies, many different crude oil samples have been used. To some extent, the tests performed on a particular sample reflect the evolution of our understanding of crude oil wetting. Sample amounts, from milliliters to barrels, also influenced the extent of testing, as does sample pedigree, i.e. to what extent were samples protected from exposure to well treatment chemicals and oxidation.

Crude Oil	Source	ρ at 25°C g/cm ³	μ at 25°C cp	Asphaltenes (wt%) precipitated by:		
				n-C ₅	n-C ₆	n-C ₇
A-90	Prudhoe Bay	0.8797	15.1	6.7	2.3	
A-93	Prudhoe Bay	0.8945	26.7	10.9	7.1	
A-95	Prudhoe Bay	0.8965	33.8	5.0		
Moutray	W.Texas	0.8426	6.2			
Schuricht	Wyoming	0.8995	31.5	9.9	8.4	
ST-86	North Sea	0.8748	13.5			
Sulimar Queen	New Mexico	0.8381	7.1	4.1		1.4

Table A-2. Gravity, acid, and base numbers.			
Crude oil	°API	Acid number (mg KOH/g oil) ¹	Base number (mg KOH/g oil) ²
A-90	28.1	0.24 ± 0.04 [*]	1.99 ± 0.09
A-92	23.8	na	na
A-93	25.5	0.14 ± 0.04 [*]	2.42 ± 0.33
A-93 ^{**}	"	0.12 ± 0.02	2.80 ± 0.08
A-95	25.2	0.24 ± 0.05 [*]	2.20 ± 0.01
Brookhaven	32.3	0.18 ± 0.03	0.46 ± 0.05
California	28.5	0.39 ± 0.03 [*]	5.19 ± 0.10
CS	25.1	0.33 ± 0.03	1.16 ± 0.18
CV	12.5	1.29 ± 0.08	2.81 ± 0.11
Dagang	27.8	0.66 ± 0.08 [*]	4.67 ± 0.17
EMSU	32.0	0.55 ± 0.02	0.80 ± 0.04
Lagrove	41.3	0.29 ± 0.02 [*]	0.65 ± 0.02
Maljamar	36.0	0.12 ± 0.04	0.72 ± 0.06
Moutray-1	35.2	0.55 ± 0.10	0.81 ± 0.09
Moutray-2	30.6	0.72 ± 0.06	0.90 ± 0.11
NBU	42.7	0.09 ± 0.03	0.56 ± 0.02
Schuricht	24.6	0.28 ± 0.12 [*]	2.09 ± 0.06
Spraberry-fresh	36.5		
Spraberry-weathered	31.1	0.32 ± 0.02	2.83 ± 0.05
ST-86	29.0	0.48 ± 0.06	1.07 ± 0.07
ST-87	27.8	0.29 ± 0.06	1.17 ± 0.01
ST-88	31.5	0.24 ± 0.01	0.53 ± 0.06
ST-89	26.5	0.10 ± 0.01	0.92 ± 0.01
Sulimar Queen-94	36.1	0.45 ± 0.05 [*]	0.24 ± 0.14
Sulimar Queen-96	37.2	0.16 ± 0.03 [*]	0.62 ± 0.03
Tensleep	31.2	0.16 ± 0.03	0.96 ± 0.01
Wassan	30.9	0.32 ± 0.09	0.97 ± 0.06

¹ ASTM D664-89
² ASTM D2896-88
^{*} some precipitate observed
^{**} measured by Triton Analytics, no precipitate reported

Brine Compositions and Properties

Buffers of varying ionic strength are made by dilution with water or by addition of NaCl to the following solutions:

Table A-3. Compositions of 0.2 M buffer solutions.					
Target pH	Acidic species			Basic species	
	ml	M	chemical	ml	chemical
4	205.0	0.2	acetic acid	45.0	sodium acetate
5	75.0	0.2	acetic acid	175.0	sodium acetate
6	15.4	0.2	sodium phosphate, dibasic	109.6	sodium phosphate, monobasic
7	76.3	0.2	sodium phosphate, dibasic	48.8	sodium phosphate, monobasic
8	118.4	0.2	sodium phosphate, dibasic	6.6	sodium phosphate, monobasic
10	33.0	0.2	sodium bicarbonate	58.9	sodium carbonate

For all work on flat surfaces, 100 mg/L of sodium azide (NaN_3) were added to the buffers as a biocide. Measured pH values vary from the target values, depending on total ionic strength of the solution. Some comparisons between nominal and actual pH are given in Table A-4, along with other physical properties measured for a variety of buffered brines. Composition of the A-93 simulated reservoir brine is given in Table A-5. Sulimar Queen synthetic brine composition is given in Table A-6.

Table A-4. Some physical and interfacial properties of NaCl buffers.								
target	pH meas'd	[NaCl]	density g/cm ³	Oil/brine IFT (mN/m)				
				A-93	A-90	Moutray	Schuricht	ST-86
4	4.1	0.01	0.9973	25.1	17.7	19.0	18.6	21.4
4	4.1	0.1	1.0026	23.5				
4	3.9	1	1.0382	21.5				
6	6.3	0.01	0.9971	26.8	16.1	16.4	19.0	19.0
6	6.3	0.1	1.0032	25.9				
6	5.7	1	1.0386	26.2				
8	7.5	0.01	0.997	26.5	13.8	12.9	18.3	21.0
8	7.7	0.1	1.0035	20.3				
8	7.2	1	1.0417	25.5				
10	10	0.01	0.9969	24.4	2.3	1.1	6.2	>1
10	9.9	0.1	1.0043	22.1				
10	9.4	1	1.0392	20.5				

Table A-5. Composition of A-93 simulated reservoir brine.		
Salt	Concentration	
	g/L	moles/L
NaCl	21.30	0.364
KCl	0.10	0.001
CaCl ₂	0.30	0.003
MgCl ₂	0.09	0.001

Table A-6. Composition of Sulimar Queen simulated reservoir brine.	
Salt	Concentration
	g/L
NaHCO ₃	0.282
Na ₂ SO ₄	4.303
CaCl ₂ ·6H ₂ O	7.776
MgCl ₂ ·6H ₂ O	74.612
NaCl	262.314

Appendix B

SURFACE TEST PROCEDURES: ADHESION AND ADSORPTION

Wetting in COBR systems is time and history dependent. The angle at the three-phase line of contact is the basis for several tests that focus on different steps in the evolution of COBR wetting. Adhesion may be observed after only a short period of exposure of solid to crude oil and is the basis of a qualitative test. Adsorption and desorption of crude oil components can occur over longer periods of exposure. Contact angles between pure fluids are measured to characterize surfaces that have been exposed to crude oils.

Contact angle measurements have been widely used as means of assessing the wetting of a surface contacted with crude oil (Anderson, 1986b). There are well-documented difficulties with the use of contact angles including:

- mineralogical differences between pore surfaces and the solids on which contact angles are measured (usually quartz or calcite),
- the effects of surface roughness,
- hysteresis, leading to contact angles that are not unique, and
- concerns about the effects of contaminants, including oxygen, on the outcome of contact angle experiments.

Recognizing these limitations, the tests described here have been designed to be reproducible and relevant specifically to COBR wetting. They are intended, not to predict wetting in a specific reservoir, but rather as tools for exploring the wettability altering propensities of different crude oils. They provide insight into the changes in wetting that are too complex to be inferred from experiments in cores.

Conventions

In order to avoid confusion in descriptions of experiments during which wetting may change, water is designated as the reference phase. Contact angles are those measured through the water phase, regardless of which phase is wetting. In this context, advancing means water is advancing over an

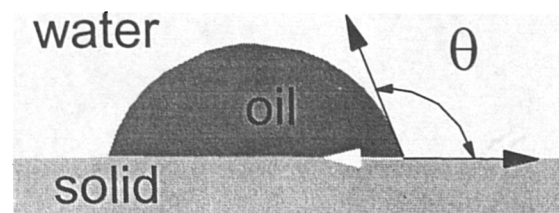


Figure B-1. The contact angle θ is defined with reference to the water phase.

oil-covered surface and receding is the opposite, water is receding as oil advances. This convention is by no means universal, but it does seem to be the simplest solution for the semantics problems that arise with regard to COBR wetting.

Adhesion

COBR contact angles measured by the captive drop technique (Gaudin, 1964) or by drops trapped between parallel plates (Leach, *et al.*, 1962) exhibit large hysteresis between receding and advancing conditions. The phenomenon that forms the basis of the adhesion test was described by Morrow, *et al.* (1986) and given a rational basis in DLVO theory by Buckley, *et al.* (1989). The test itself is deceptively simple. A drop of oil is formed under water, at the tip of either a microburette or syringe, held as rigidly as possible to avoid vibration during changes in drop volume. The volume of the oil droplet can vary, but it is usually quite small (a few μl or less). Variations in contact angle with drop volume are of secondary importance in these measurements. The oil droplet is allowed to contact a smooth solid surface, also submerged in the aqueous phase. After some period of contact between oil and solid, the drop is drawn back into the needle or buret tip. At that stage, very different phenomena have been observed, as illustrated in Fig. B-2, for the two extremes of possible outcomes.

In some cases, referred to here as nonadhesion, there is very little difference between advancing and receding contact angles (θ_a and θ_r , respectively). At the other extreme, the three phase contact line is pinned, and, as the volume of the oil drop is reduced, the shape of the drop is distorted, as shown

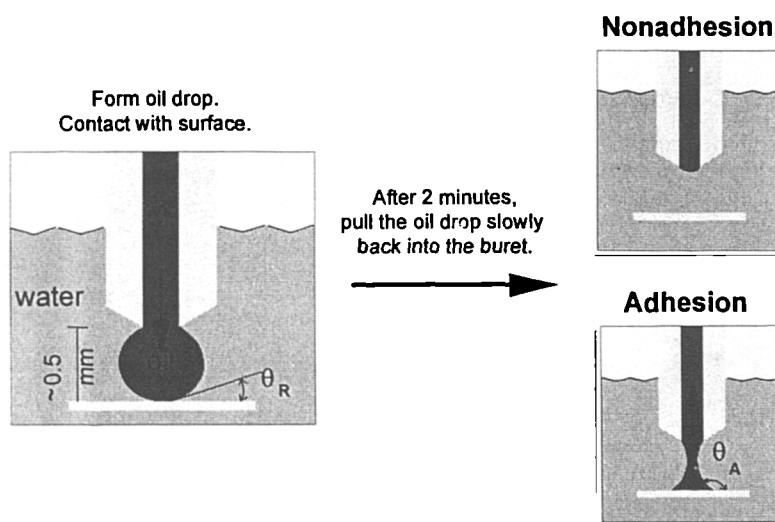


Figure B-2. Illustration of adhesion and nonadhesion between an oil droplet and solid surface under water.

in the case labeled adhesion. Further reduction in the drop volume results in separation of the adhering drop from the oil in the reservoir. Drops of oil up to about 0.5 μl in volume may remain adhering to the surface. Using this simple distinction between adhering and

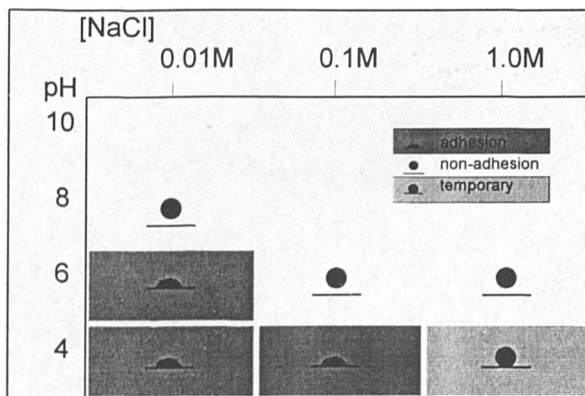


Figure B-3. A typical adhesion map delineates conditions of NaCl concentration and pH in which adhesion occurs (A-93 crude oil, measured at 80°C).

nonadhering conditions, a map of brine compositions can be made with distinctions drawn between areas of adhesion and nonadhesion. A typical example is shown in Fig. B-3. An intermediate condition (temporary adhesion) is often observed in which θ_A is high, the oil droplet adheres, and breaks off. With time, however, the contact angle begins to decrease and eventually the drop is released and floats to the surface.

Dividing the observations into two or three categories gives a clear picture of the striking differences that, for most combinations of crude oils and NaCl solutions, depend primarily on solution pH and secondly on ionic strength. The physical properties of the oil/water and solid/water interfaces that underlie these observations are discussed in detail in Chapter 3.

Of course, this arbitrary division according to the extremes of adhesion and nonadhesion is an oversimplification. A great deal of additional detail can be observed in these tests. The three phase line is not always pinned, but may slip at a well-defined advancing contact angle. The volume and final contact angle of adhering drops can vary. In principle, the adhering drop might spread. This situation has been observed only once (i.e. for one crude oil in contact with a single brine composition) in many hundreds of these measurements with dozens of different crude oils. Variations in the standard procedure, for example allowing longer contact times, can provide additional information, but the standard procedure provides a fixed point in this universe of variables from which to begin.

Standard procedure for the adhesion test: The steps involved in the standard adhesion test are outlined in Fig. B-4. Thorough washing of the surface is an obvious first

step. Less obvious is the extent to which the washing step can bias the adhesion results because of its influence on the initial surface charge of the glass or mineral surface. This initial charge state can be quite different for surfaces washed with concentrated acid or with caustic solutions. Both cases would be clean, in the sense of being free of organic contamination, and strongly water-wet, but it is the surface charge conditions that are of greatest importance in the adhesion test.

There is no one correct starting point, of course, but to achieve results that

are reproducible and comparable with one another, it is important that the starting conditions be as constant as possible. This is achieved by standardizing the washing procedure, by rinsing very thoroughly, and by soaking the surfaces for several days in aqueous solution before the adhesion test proceeds. For microscope glass slides and other silica surfaces, trial and error has shown that reproducible results can be obtained by cleaning with ultrasonic agitation for 15 to 30 minutes in a cleaning solution that is a mixture of nine parts hydrogen peroxide (30%) and one part ammonium hydroxide (20%). This washing procedure has been adopted for the standard adhesion test. Use of surfaces other than silica may require some adaptation of this initial step.

After many rinses with glass distilled water, the solid samples are equilibrated with the measurement brine for a period from three days to two weeks. Surface charge is changing rapidly during the first few hours (Kulkarni and Somasundaran, 1973) and is more stable after two or three days. A minimal amount of biocide (100 ppm of NaN_3) is used to deter biological activity in the aqueous solutions, but their useful period is limited nevertheless. The standard adhesion test scans brine compositions from 0.01 to 1.0 M NaCl and from pH 4 to 8. Brines are weakly buffered and pH is recorded when they are prepared and again when the measurements are made.

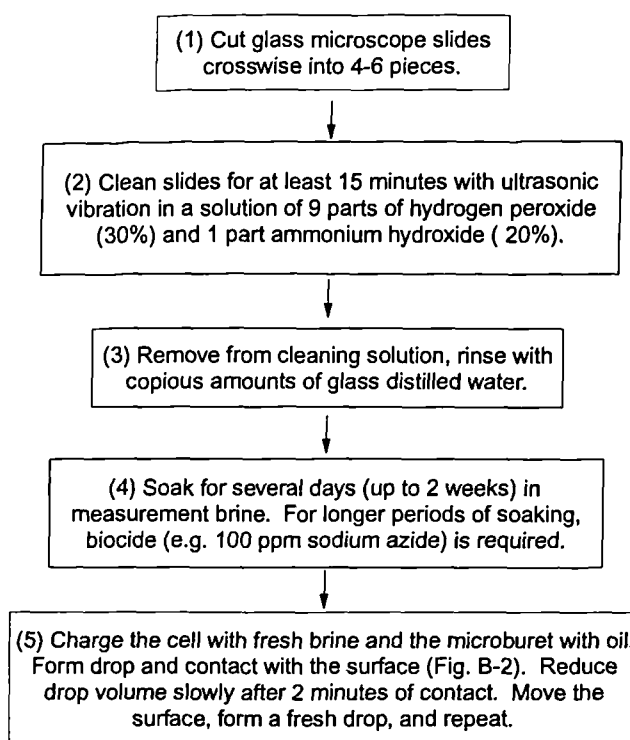


Figure B-4. Outline of the standard adhesion test.

The standard contact time for an oil drop trapped between the buret and the solid surface is two minutes. Longer times are often checked, especially in transition regions, but better temperature control is required as the measurement time increases. Many measurements are made on each surface and on duplicate surfaces as well. The possibility of cooperative effects, where contact with the first drop of oil affect subsequent measurements, are considered, but have not been observed.

Enhancements to the standard adhesion test: The standard test is really just the beginning, a base-line of data for comparing different crude oils. Detail in the adhesion map depends on the number of brine compositions (of specified pH and ionic strength) tested. Salts other than NaCl may be used, including those with divalent and multivalent ions. Temperature can be varied in an environmental cell (Rame-Hart) and with improved temperature control, there is also the option for prolonged contact times. Details beyond the simple adhesion/nonadhesion distinction, can be measured. These include the receding angle, an advancing angle (if the three-phase contact line slips), and the size of the adhering drops.

Adsorption and Desorption

In order to observe much longer periods of interaction between smooth solid surfaces, brines, and crude oils, a second standard test has been developed (Buckley and Morrow, 1991; Liu and Buckley, 1995). An outline of the standard procedure adopted for this adsorption test is shown in Fig. B-5.

Washing and equilibration with brine are the same as described above for adhesion. For comparison, some samples can be dried after

washing and aged in crude oil without first being equilibrated with brine (Chapter 2). After equilibrating in brine, the solid pieces are removed and allowed to drain, but not to dry, before being immersed in crude oil. Variables include brine and oil compositions, aging time

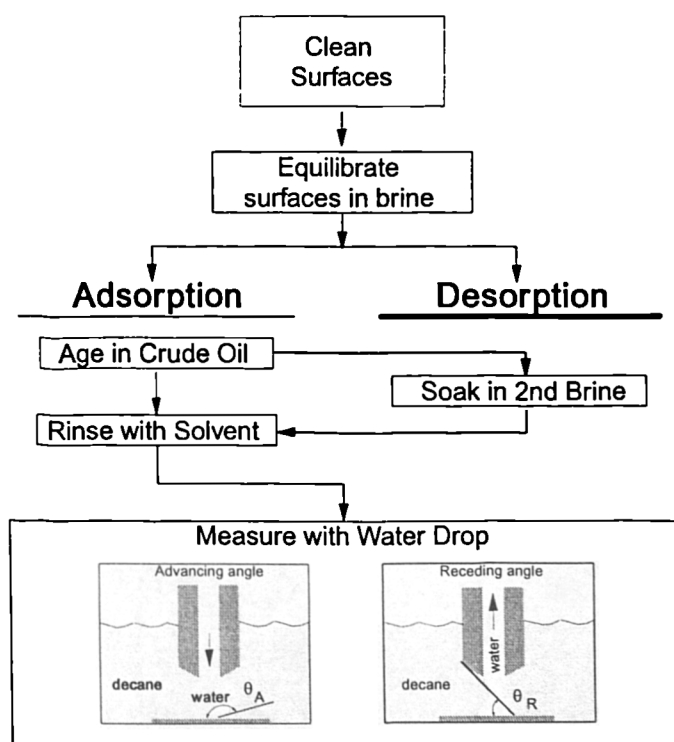


Figure B-5. Standard procedures for adsorption and desorption tests.

and temperature. At the end of the period of aging in oil, samples are removed and washed gently with solvent to remove bulk oil. Toluene has been used as the standard solvent; cyclohexane gives nearly the same results. Fluids that are poor asphaltene solvents, like decane, are avoided since they make the surfaces uniformly oil-wet (Chapter 2). After washing, the treated surface is immersed in just such a poor asphaltene solvent so that further changes are not occurring during the measurement of water advancing and receding contact angles, as illustrated in Fig. B-5.

An additional step, immersing the treated surface in another brine solution and aging again shows the extent to which the adsorbed components can be removed. Desorption varies with time, temperature, and brine composition, which may be identical to the first brine or different from it. Results of COBR adsorption and desorption experiments are presented and discussed in Chapter 3.

Comparison of Adhesion and Adsorption

Although these two tests seem similar, each involving observations of captive drops on solid surfaces, they are different in some important respects. In the adhesion experiment, a drop of crude oil contacts a clean, brine covered surface. The area under the drop of oil is unevenly contacted because of the dimple of water that is trapped under the oil drop (Joye *et al.*, 1992). In the cases where adhesion of a drop is observed, the three-phase contact line can be pinned. Longer contact times can exacerbate the pinning problem. Finally, the advancing angle probably represents water advancing over a bilayer of oil components, as shown in Fig. B-6.

In order to avoid pinning and to observe interactions that may occur over long periods of time, the adsorption test protocol was developed. Longer adsorption times are readily achieved, but in order to assess changes in the solid surface, presumable due to adsorption of material from the crude oil, bulk oil must first be removed. This necessitates dilution of the oil with solvents and means that the contact angle measured reflects the residual or remaining effect after washing off the bulk crude oil. This process is envisioned to produce contact angles as shown in Fig. B-7.

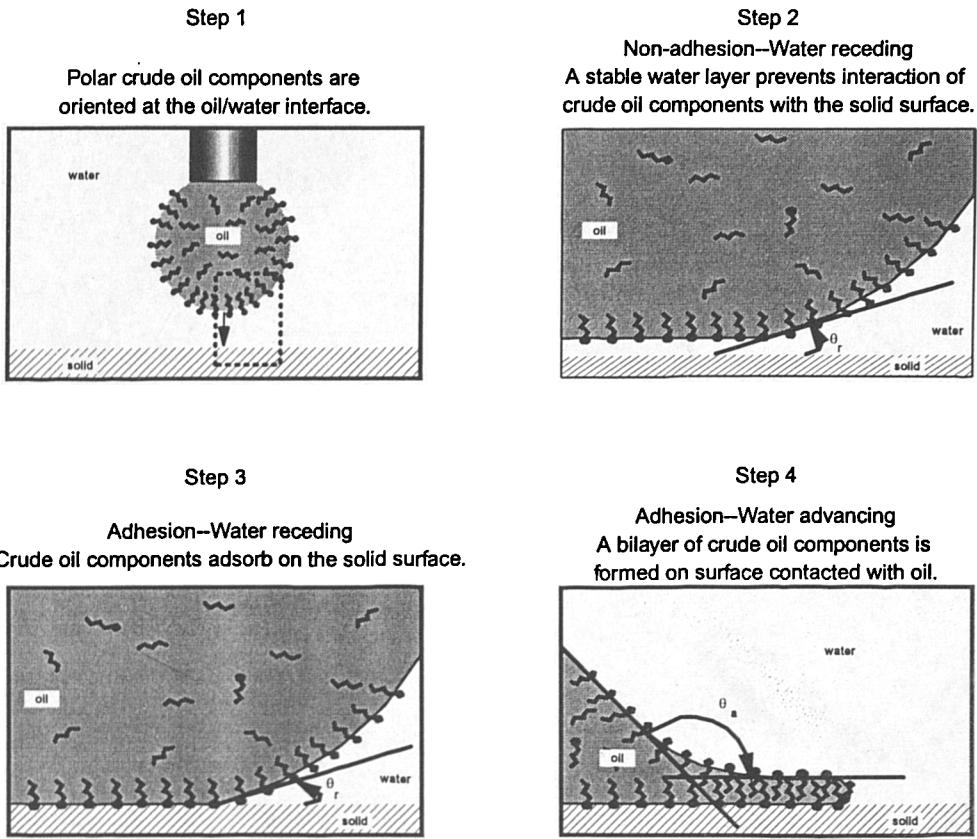


Figure B-6. Adhesion under water of a crude oil droplet on a smooth solid surface.

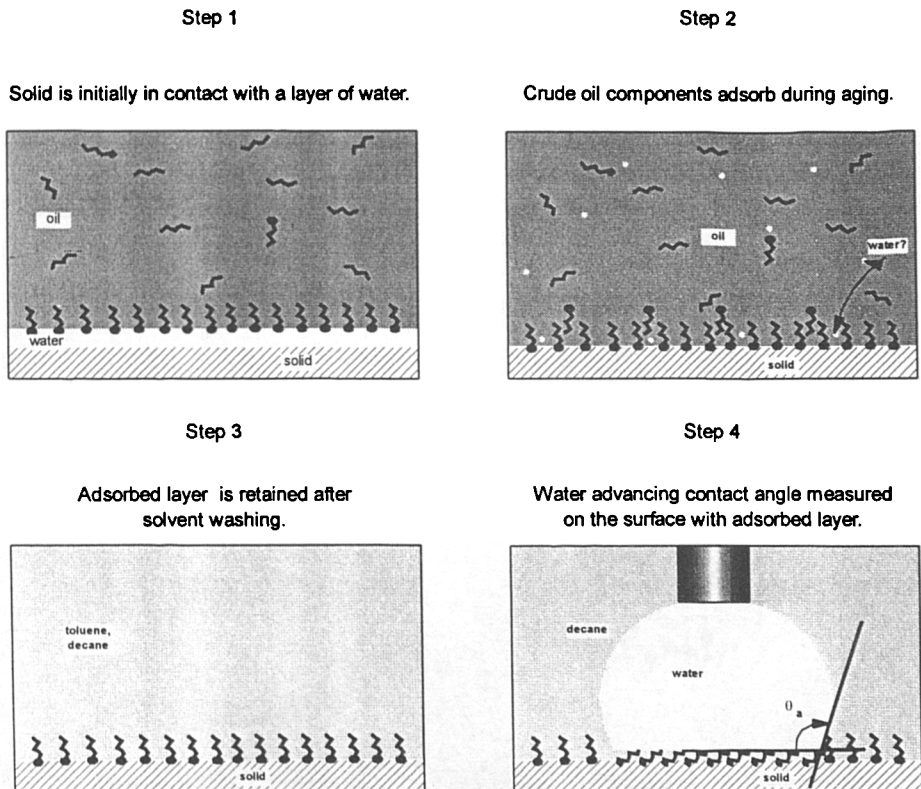


Figure B-7. Changes in solid surface during the adsorption test.

Appendix C

INTERFACIAL CHARGE CALCULATIONS

The equations and assumptions used in making calculations of interfacial charge and zeta potential are summarized in this appendix.

The ISG Model

The concentrations of ions near a charged surface (or interface) different than the concentrations in the bulk fluid. Surface charge density, bulk concentrations of the ions in solution, their valence and sign, and distance from the charged interface are all important variables. For a surface with ionizable sites, the surface charge density depends, in turn, on the surface concentrations of some of the ions in solution. In the case of dissociation of acidic and basic species, the hydrogen ion concentration at the surface shifts the position of equilibrium and thus the surface charge. If the numbers and dissociation constants of the ionizable sites are known, conditions that satisfy both the dissociation equations and the Boltzmann distribution can be found.

Crude oils have both basic (positive) and acidic (negative) ionizable sites. The numbers and dissociation constants of these interfacially active sites cannot be measured directly, but they can be inferred from changes in interfacial properties including IFT and electrophoretic mobility with brine composition. In Chapter 2, the ISG model was tested with data from interfaces with known ionizable compounds (either acidic or basic). The equations used to calculate surface charge as a function of the types and numbers of ionizable sites (see Buckley *et al.*, 1989, and references cited therein) are collected here for reference.

Assume a charged surface has acidic ionizable sites, then the equilibrium equation is



and the dissociation constant is

$$K_a = \frac{[A^-][H^+]}{[AH]}$$

There is some distribution of acidic sites between the species AH and A⁻. Adding H⁺ (decreasing the pH) shifts the equilibrium toward the AH or protonated form. Up to this point, the process is identical to dissociation of a weak acid in solution. The difference between bulk solution and a charged surface is that near a charged surface, the concentration of cations and counterions are different than they are in the bulk solution.

If we assume that the dissociation equilibrium is essentially the same, we can substitute in the equations the hydrogen ion concentration *at the surface* which can be related to the bulk concentration by the Boltzmann distribution:

$$\rho_{o,i} = \rho_{\infty,i} \exp\left(\frac{-z_i e \psi_o}{kT}\right)$$

where $\rho_{o,i}$ is the concentration of species *i* at the surface (molecules/m³)
 $\rho_{\infty,i}$ is the concentration of species *i* in the bulk solution (an infinite distance from the charged surface) (molecules/m³) and $\rho_{\infty,i} = 1000 N_o C_i$ where

N_o = Avogadro's number = 6.022×10^{23} molecules/mole, and

C_i is concentration of species *i* in moles/L

z_i is the valence of species *i*

ψ_o is the potential at the surface (V)

T is temperature (°K)

$-e$ = electron charge = 1.602×10^{-19} C

k = Boltzmann constant = 1.381×10^{-23} J K⁻¹

For monovalent ions, let $y_o = e\psi_o/kT$, then

$$\rho_{o,H^+} = \rho_{\infty,H^+} \cdot \exp(-y_o)$$

For a given species *i*, the concentration of *i* at the charged interface depends on ψ_o which in turn depends on the surface charge density, σ_o . Surface charge has units of C/m² and is related to the number of acids in the ionized form by:

$$\sigma_o = -e\rho_{A^-}$$

The total number of acidic sites, N_a , is the sum of ionized and protonated forms:

$$N_a = \rho_{AH} + \rho_{A^-}$$

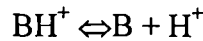
Rewriting the expression for K_a gives

$$\rho_{AH} = \frac{\rho_{A^-} \rho_{\infty, H^+}}{K_a} \exp(-y_o)$$

$$N_a = \rho_{A^-} \left(\frac{\rho_{\infty, H^+}}{K_a} \exp(-y_o) + 1 \right)$$

$$-\sigma_o = \frac{eN_a}{1 + \frac{\rho_{\infty, H^+}}{K_a} \exp(-y_o)}$$

A similar expression can be derived for charge on a surface consisting of ionizable basic sites for which the dissociation equation is:



In this case surface charge is:

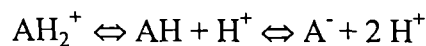
$$\sigma_o = \frac{eN_a}{1 + \frac{K_a}{\rho_{\infty, H^+}} \exp(y_o)}$$

A surface with two or more type of sites, either acidic or basic, can be specified by the number density of each type of site and its dissociation constant. In this case surface charge is given by the following expression:

$$\sigma_o = e \sum_i \left(\frac{z_i N_{ai}}{1 + \left(\frac{K_{ai}}{\rho_{\infty, H^+}} \right)^{z_i} \exp(z_i y_o)} \right)$$

where z_i is -1 for an acidic site and +1 for a basic site.

Finally there is the case of sites which can have either positive or negative charge, depending on pH. Some mineral surfaces including the silanol sites at silica surfaces have this amphoteric property. The dissociation equation can be written:



If the first dissociation has a constant, K_+ and the second is K_- then the expression for surface charge is as follows:

$$\sigma_o = eN_a \left(\frac{\frac{\rho_{\infty, H^+} \exp(-y_o)}{K_+} - \frac{K_-}{\rho_{\infty, H^+} \exp(-y_o)}}{1 + \frac{\rho_{\infty, H^+} \exp(-y_o)}{K_+} + \frac{K_-}{\rho_{\infty, H^+} \exp(-y_o)}} \right)$$

Note that there are two equilibrium constants but only one number of sites, N_a , since it is the same sites that can be either positive, neutral, or negative.

These equations can be solved iteratively to give an interfacial charge that satisfies both the equilibrium relationships and the Boltzmann distribution.

Appendix D

PROPERTIES OF ORGANIC ACIDS AND BASES

Commonly identified acidic and basic functional groups in crude oils are carboxylic acids and pyridinic nitrogen. Dissociation constants for these and other organic acids, bases and for amphoteric compounds are collected in this appendix.

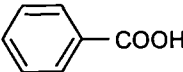
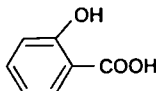
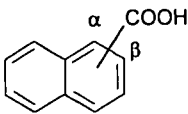
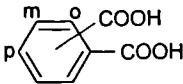
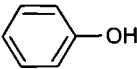
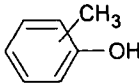

Table D-1. Organic acids.		
Compound	Structure	pK _a
acetic acid	CH ₃ - COOH	4.75
thioacetic acid	CH ₃ - COSH	3.33
n-nonanic acid	CH ₃ - (CH ₂) ₇ - COOH	4.96
benzoic acid		4.2
salicylic acid		2.94
naphthenic acid		α) 3.7 β) 4.17
adipic acid	HOOC - (CH ₂) ₄ - COOH	4.43, 5.41
phthalic acid		o) 2.89, 5.51 m) 3.54, 4.60 p) 3.51, 4.82
phenol		9.89
cresols		o) 10.20 m) 10.01 p) 10.17
resorcinol		9.81

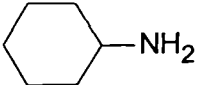
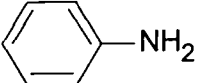
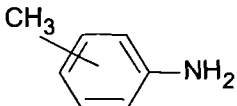
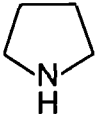
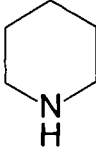
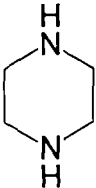
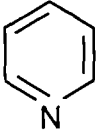
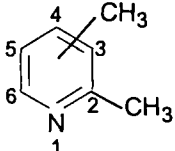
Table D-2. Organic bases.		
Compound	Structure	pK _a
n-butyl amine	$\text{CH}_3(\text{CH}_2)_3 - \text{NH}_2$	10.77
t-butyl amine	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2 - \text{C} - \text{NH}_2 \\ \\ \text{CH}_3 \end{array}$	10.83
laurel amine	$\text{CH}_3 - (\text{CH}_2)_{11} - \text{NH}_2$	10.63
dimethyl amine	$\text{CH}_3 - \text{NH} - \text{CH}_3$	10.73
cyclohexyl amine		10.66
aniline		4.63
toluidine		o) 4.44 m) 4.73 p) 5.08
pyrrolidine		11.27
piperadine		11.12
piperazine		9.83
pyridine		5.25
lutidine		2,3) 6.57 2,4) 6.99 3,5) 6.15

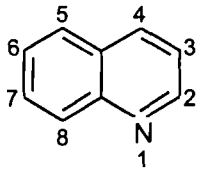
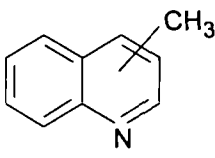
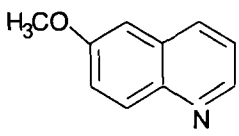
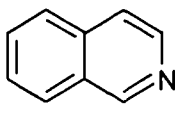
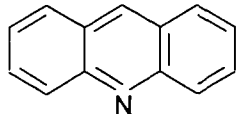
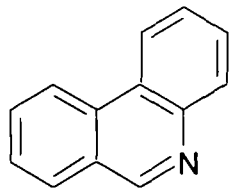
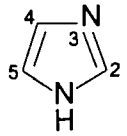
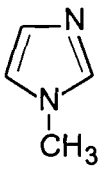
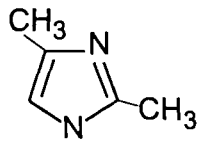
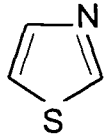
Table D-2. Organic bases.		
Compound	Structure	pK _a
quinoline		4.90
methylquinoline		2) 5.83 4) 5.67 5) 5.2
6 methoxy-quinoline		5.03
isoquinoline		5.42
acridine		5.58
phenanthridine		5.58
imidazole		6.95
1-methyl-imidazole		6.95
2,4-dimethyl-imidazole		8.36
thiazole		2.44

Table D-2. Organic bases.

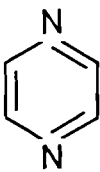
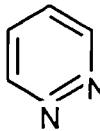
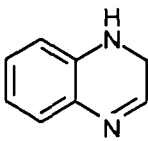
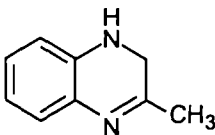
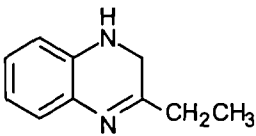
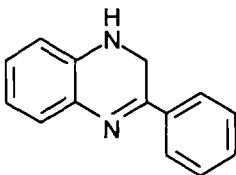
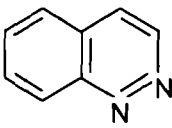
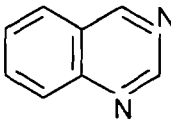
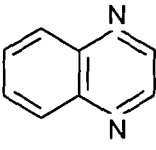
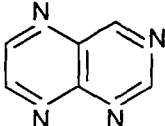
Compound	Structure	pK _a
pyrazine		0.65
pyridazine		2.24
benzimidazole		5.53
2-methyl-benzimidazole		6.19
2-ethyl-benzimidazole		6.18
2-phenyl-benzimidazole		5.23, 11.91
cinnoline		2.37
quinazoline		3.43
quinoxaline		0.56
pteridine		4.05

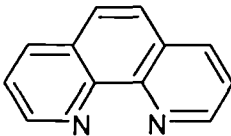
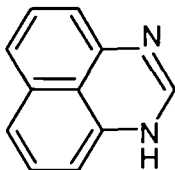
Table D-2. Organic bases.		
Compound	Structure	pK _a
1,10-phenanthroline		4.84
perimidine		6.35

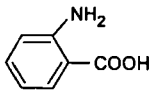
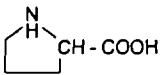
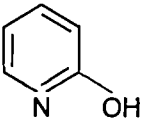
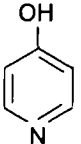
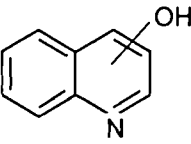
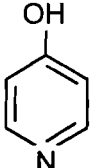
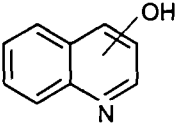
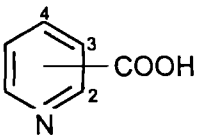
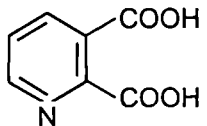
Table D-3. Amino acids.		
Compound	Structure	pK _a
glycine (Gly) pI = 5.97	$\begin{array}{c} ^+\text{NH}_3 \\ \\ \text{HCH} - \text{COO}^- \end{array}$	2.34, 9.60
leucine (Leu) pI = 5.98	$\begin{array}{c} \text{NH}_2 \\ \\ \text{CH}_3 \diagdown \text{CH} - \text{CH}_2 - \text{CH} - \text{COOH} \\ \text{CH}_3 \diagup \end{array}$	2.36, 9.60
α-amino caproic acid	$\text{CH}_3 - (\text{CH}_2)_3 - \begin{array}{c} \text{NH}_2 \\ \\ \text{CH} - \text{COOH} \end{array}$	2.39, 9.76
ε-amino caproic acid	$\text{H}_2\text{N} - (\text{CH}_2)_5 - \text{COOH}$	4.43, 10.75
phenylalanine (Phe) pI = 5.48	$\text{C}_6\text{H}_5 - \begin{array}{c} \text{NH}_2 \\ \\ \text{CH}_2 - \text{CH} - \text{COOH} \end{array}$	1.83, 9.13
tyrosine (Try) pI = 5.66	$\text{HO} - \text{C}_6\text{H}_4 - \begin{array}{c} \text{NH}_2 \\ \\ \text{CH}_2 - \text{CH} - \text{COOH} \end{array}$	2.20, 9.11, 10.07
anthranilic acid		2.11, 4.95
serine (Ser) pI = 5.68	$\text{HO} - \text{CH}_2 - \begin{array}{c} \text{NH}_2 \\ \\ \text{CH} - \text{COOH} \end{array}$	2.21, 9.15
cysteine (Cys) pI = 5.07	$\text{HS} - \text{CH}_2 - \begin{array}{c} \text{NH}_2 \\ \\ \text{CH} - \text{COOH} \end{array}$	1.96, 8.18, 10.28
methionine (Met) pI = 5.74	$\text{CH}_3 - \text{S} - \text{CH}_2 - \text{CH}_2 - \begin{array}{c} \text{NH}_2 \\ \\ \text{CH} - \text{COOH} \end{array}$	2.28, 9.21
proline (Pro) pI = 6.3		1.99, 10.60
tryptophan (Trp) pI = 5.89	$\text{C}_8\text{H}_6\text{N}_2 - \begin{array}{c} \text{NH}_2 \\ \\ \text{CH}_2 - \text{CH} - \text{COOH} \end{array}$	2.38, 9.39
aspartic acid (Asp) pI = 2.77	$\text{HOOC} - \text{CH}_2 - \begin{array}{c} \text{NH}_2 \\ \\ \text{CH} - \text{COOH} \end{array}$	1.88, 3.65, 9.60
gluamic acid (Glu) pI = 3.22	$\text{HOOC} - \text{CH}_2 - \text{CH}_2 - \begin{array}{c} \text{NH}_2 \\ \\ \text{CH} - \text{COOH} \end{array}$	2.19, 4.25, 9.67

Table D-4. Amphoteric with heterocyclic, aromatic nitrogen.

Compound	Structure	pK _a
2-hydroxypyridine (2 Pyridol)		0.75, 11.65
4-hydroxypyridine		3.20, 11.12
hydroxyquinoline		3) 4.28, 8.08 8) 5.02, 9.81
7-hydroxyisoquinoline		5.68, 8.90
5-hydroxyquinazoline		3.62, 7.41
pyridine carboxylic acids		
2) picolinic		2) 0.99, 5.39
3) nicotinic		3) 1.77, 4.84
4) isonicotinic		4) 2.00, 4.82
quinolinic acid		2.52

Appendix E

PROCEDURES FOR COREFLOODS AND IMBIBITION TESTS

The procedures used to test cores in this work have two main purposes: to assess the extent of wetting alteration by COBR interactions and to show the effects of wetting alteration on recovery of oil by waterflooding. These are fairly standard tests, although the details of test procedures can affect their outcome significantly. In this appendix, these procedures are documented.

Initial Core Preparation

Cylindrical cores are cut with a diamond core bit, using tap water for cooling. They are allowed to dry for several days in an oven at 80°C, after which nitrogen permeabilities are measured. Selected core plugs are saturated under vacuum in degassed brine and allowed to equilibrate in the brine phase for one week at ambient temperature. At the end of this equilibration time, absolute permeability to brine is measured. Synthetic and outcrop cores thus prepared are strongly water-wet, and are ready for use in various kinds of experiments.

Wetting Alteration by COBR Interactions

For alteration of core wettability, the brine-saturated cores are flooded with crude oil to establish an initial water saturation. An initial measurement of oil permeability is made. The value of initial water saturation, aging time, and aging temperature are the main variables associated with the extent of wetting alteration at this stage. Cores with oil and connate water are submerged in crude oil in a sealed beaker and stored either in an oven or a water bath at the designated aging temperature. At the end of the aging period, the oil aged in the core is displaced with fresh oil, either the same crude or a refined oil, and permeability to oil with connate water in place is remeasured.

Core Cleaning

Occasionally cores are cleaned after contact with crude oil, although there is no expectation that cleaning will always be successful in returning cores to their original state. The procedure that used was first to remove crude oil by flushing the core with toluene until the effluent is clear. At each step flow was halted overnight and clarity of the effluent was

tested again the next day. The second step was to flush with a mixture of 50% toluene and 50% isopropanol. Finally cores were flushed with isopropanol alone.

Imbibition

The use of imbibition measurements to characterize wettability in cores has been common since a test was proposed by Amott (1959) that compared the amount of a phase imbibed spontaneously with the amount of that phase taken up by the same core in a forced displacement. While this is strictly an empirical measure that can be affected by many experimental details, it does provide a framework for comparisons from one sample to another and even from one rock type to another. The procedure used here is similar to that suggested by Cuiec (1984, 1991). It combines spontaneous imbibition with viscous forced displacement in a coreflood, as opposed to the gravity-driven centrifuge displacement recommended by Amott. An idealized capillary pressure curve is shown in Fig. E-1 with the saturations used to calculate wetting parameters indicated. Since only endpoint saturations are used, measurement of P_c is not required.

All steps shown by solid lines in Fig. E-1 are viscous displacements with the core confined in a Hassler holder (as described below). In the spontaneous imbibition steps (dotted lines), all core surfaces are exposed to the imbibing fluid. Imbibition is monitored gravimetrically (Morrow, *et al.*, 1986) as shown in Fig. E-2.

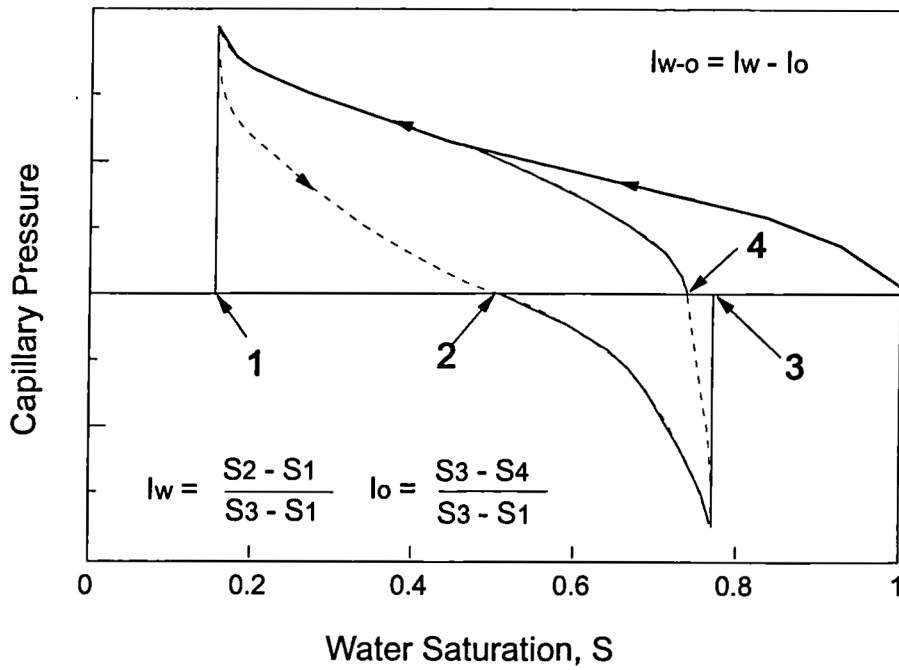


Figure E-1. Idealized capillary pressure vs. saturation curve, indicating the values used for calculation of Amott wettability indices (I_w and I_o) and the combined Amott-Harvey index I_{w-o} .

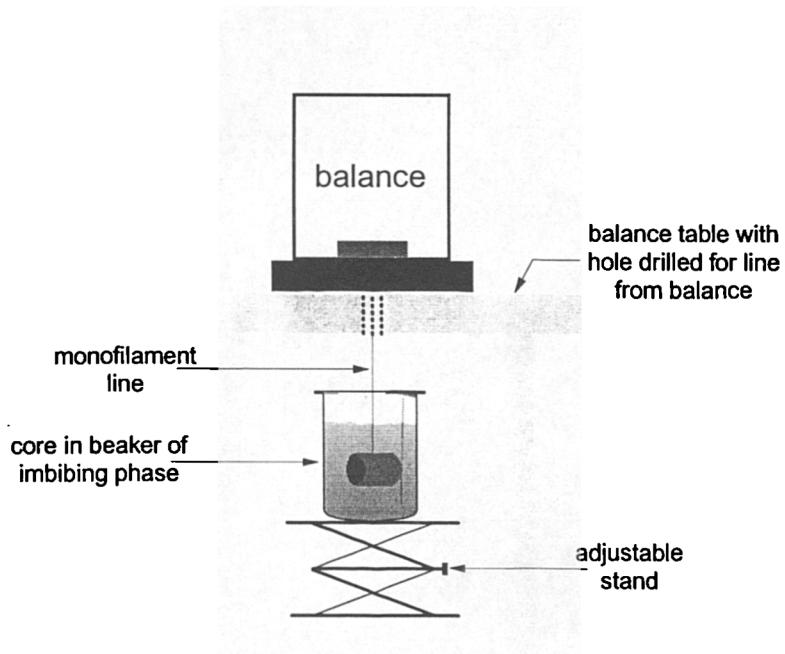


Figure E-2. Setup for gravitational monitoring of rate of imbibition into suspended cores.

Waterflooding

Waterfloods are performed at constant flow rate with the core confined in a Hassler holder as illustrated in Fig. E-3 with about 300 psi of confining pressure provided by nitrogen. Pressure is monitored with a transducer upstream of the core. The outlet pressure is atmospheric.

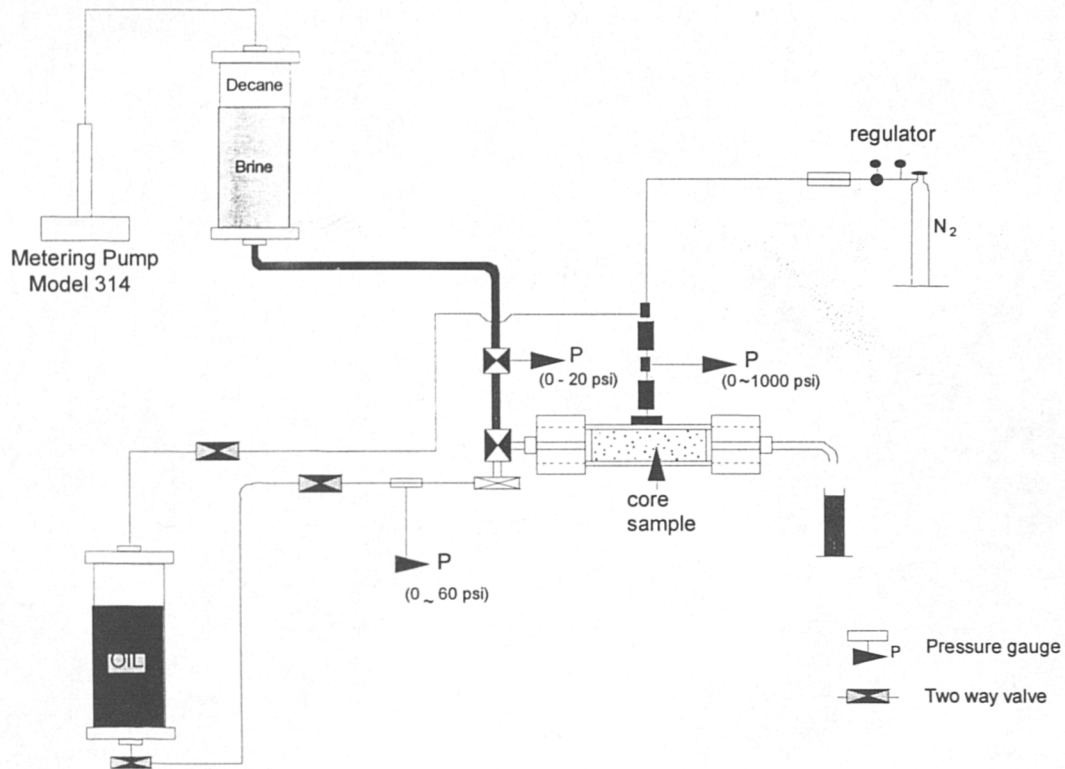


Figure E-3. Waterflood apparatus for constant rate experiments.

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