

WETTING ALTERATION OF SOLID SURFACES BY CRUDE OILS AND THEIR ASPHALTENES

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MODIFICATION DE LA MOUILLABILITÉ
DES SURFACES SOLIDES PAR LES PÉTROLES BRUTS
ET LEURS ASPHALTÈNES

Les pétroles bruts contiennent de nombreux constituants — dont les asphaltènes — qui peuvent être adsorbés sur les surfaces minérales et modifier leurs caractéristiques de mouillage. Ce qui distingue les asphaltènes des autres constituants de l'huile est leur tendance à s'agréger et même à se séparer du pétrole en réaction à des modifications du pouvoir solvant du pétrole. Du fait qu'ils changent de taille, les asphaltènes peuvent être considérés soit comme des macromolécules, soit comme des colloïdes. Leur influence sur la mouillabilité peut varier selon que le régime est plutôt moléculaire ou plutôt colloïdal.

En tant que macromolécules, les asphaltènes et les autres constituants du pétrole possédant des fonctions polaires peuvent s'adsorber sur les surfaces minérales. Il est établi que de nombreux pétroles différents modifient la mouillabilité de surfaces silicatées sèches de façon similaire. En présence d'eau, toutefois, les résultats de l'exposition de surfaces à différentes huiles peuvent être fort complexes, en fonction de la distribution de l'eau, des compositions de l'huile et de l'eau, et de la minéralogie des surfaces. Les indices d'acidité et de basicité, ainsi que les relations entre ces deux paramètres procurent une mesure de la faculté d'une huile donnée à modifier la mouillabilité par des mécanismes ioniques. En tant que colloïdes, les asphaltènes peuvent modifier la mouillabilité par un mécanisme supplémentaire. Au voisinage du seuil de précipitation, le changement de mouillabilité intervient par précipitation superficielle à cause de l'aggrégation des asphaltènes colloïdaux à l'interface, qui peut précéder la floculation d'ensemble. L'influence des asphaltènes sur la mouillabilité dépend donc fortement de l'environnement dans lequel ils se trouvent. L'indice de réfraction du mélange est une mesure utile pour quantifier la stabilité des asphaltènes dans un pétrole brut et donc, aussi, pour séparer les contributions moléculaire et colloïdale dans les changements de mouillabilité induits par les asphaltènes

WETTING ALTERATION OF SOLID SURFACES
BY CRUDE OILS AND THEIR ASPHALTENES

Crude oils contain a variety of components—including asphaltenes—that can adsorb onto mineral surfaces and alter wetting. What distinguishes the asphaltenes from other constituents of an oil is their tendency to aggregate and even separate from the oil in response to changes in oil solvency. Because they change in size, asphaltenes can be viewed as both

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macromolecules and colloids. Their influence on wettability can change with this shift from molecular to colloidal regimes.

As macromolecules, asphaltenes and other crude oil components with polar functionality can adsorb on mineral surfaces. Many different crude oils have been shown to have similar effects on wetting of dry silicate surfaces. When water is present, however, the results of exposing surfaces to different oils can be quite complex, depending on the distribution of water, the compositions of oil and brine, and mineralogy of rock surfaces. Acid and base numbers and the relationship between them provide a measure of the potential for a particular oil to alter wetting through ionic interactions. As colloids, asphaltenes can alter wetting by an additional mechanism. Near the onset of precipitation, wetting alteration occurs by surface precipitation because of the interfacial aggregation of the colloidal asphaltenes, which can precede flocculation in bulk. The influence of asphaltenes on wetting is thus strongly dependent on the environment in which they are found. Mixture refractive index is a useful measure for quantifying the stability of asphaltenes in a crude oil and thus in differentiating between macromolecular and colloidal contributions of asphaltenes to wetting alteration.

MODIFICACIÓN DE LA HUMECTABILIDAD DE LAS SUPERFICIES SÓLIDAS POR LOS PETRÓLEOS CRUDOS Y SUS ASFALTENOS

Los petróleos crudos contienen numerosos componentes — entre los cuales los asfaltenos — que pueden ser adsorbidos en las superficies minerales y modificar sus características de humectación. Los asfaltenos se distinguen de los demás componentes del petróleo debido a su tendencia de agregarse e incluso separarse del petróleo como reacción a las modificaciones del poder disolvente del petróleo. Debido a la alteración de sus dimensiones, los asfaltenos se pueden considerar, ya sea como macromoléculas o bien, como coloides. Su influencia respecto a la humectabilidad puede variar según si el régimen es más bien molecular o más bien coloidal.

Considerados como macromoléculas, los asfaltenos y los demás componentes del petróleo poseen funciones polares que pueden adsorberse en las superficies minerales. Se ha establecido que numerosos petróleos diferentes modifican la humectabilidad de superficies silicatadas secas, y ello de forma similar. No obstante, en presencia de agua los resultados de la exposición de superficies a la acción de distintos petróleos pueden llegar a ser sumamente complejas, en función de la distribución del agua, de las composiciones del petróleo y del agua, así como de la mineralogía de las superficies. Los índices de acidez y de basicidad, así como las relaciones entre ambos parámetros, proporcionan una medida de la facultad de un petróleo determinado para modificar la humectabilidad por la acción de mecanismos iónicos. Considerados como coloides, pueden modificar la humectabilidad, al intervenir por precipitación superficial debido a la agregación de los asfaltenos coloidales en el interfaz, que puede preceder la floculación de conjunto. La influencia de los asfaltenos con respecto a la humectabilidad depende por consiguiente, y en gran proporción, del entorno en el cual se encuentran los asfaltenos. El índice de refracción de la mezcla constituye una medida útil para cuantificar los asfaltenos en un petróleo crudo y, por ende, también para separar la contribución molecular y coloidal en las modificaciones de la humectabilidad inducidas por los asfaltenos.

INTRODUCTION

Wetting conditions in oil reservoirs have been the subject of many different kinds of studies. The extensive literature in this area has been the subject of several reviews (Anderson, 1986; Morrow, 1990; Cuiec, 1991). Asphaltenes, which include the heaviest and most polar components in an oil, are generally assumed to have the greatest impact on wetting. However, quantifying the effects of asphaltenes on wetting is problematic.

Simply defining asphaltenes constitutes the first hurdle. There is no single, generally accepted definition of asphaltenes. Materials from different sources may have very different properties. Even those derived from a single source may have different wettability altering characteristics if different isolation methods have been used. If asphaltenes have been separated from oil, they are generally redissolved in toluene or other organic solvents. Their wettability altering properties can vary from one solvent environment to another.

Quantifying the asphaltene/solid interactions is another important problem. Adsorption isotherms have provided information about adsorption mechanisms and the amount of material involved. Alteration of surface properties has often been shown by changes in contact angles on flat surfaces. In porous media, indirect measures of wetting are mainly based on the rate and amount of an immiscible fluid that imbibes spontaneously.

Attempts to relate one measure to another or to generalize about the effects of asphaltenes on wetting reveal many inconsistencies. In part, confusion arises because asphaltenes can influence wetting by more than one mechanism. In the remainder of this paper, we will review the evidence pertaining to the effects of asphaltenes on wetting and resolve some of the apparent inconsistencies through improved definition of the mechanisms by which asphaltenes can influence wettability.

1 DEFINITIONS OF ASPHALTENES

Lack of agreement regarding the definition and nature of the asphaltenes has fueled many disputes, without resolving the role that asphaltenes play in establishing wetting conditions in oil reservoirs. It is now well accepted that asphaltenes do not constitute a chemically distinct class. They include a broad range of

chemical species, generally of high molecular weight, aromaticity, and polarity (Long, 1981; Cimino *et al.*, 1995).

There are many similar standard procedures for separating asphaltene (e.g., ASTM D2007-80), all based on the insolubility of asphaltene in low molecular weight paraffins. Usually 1 g of oil is diluted with 40 ml of *n*-pentane (or *n*-heptane). After allowing some time for flocculation, the asphaltene is separated by filtration and washed with additional pentane (or heptane) to remove any resins or other oil components that tend to coprecipitate. Choice of precipitant, volumes of oil and precipitant, precipitation time, and washing procedure can influence the amount and composition of the separated material. Hence standardization is necessary if the results are to be comparable from one laboratory to another. However, a standard procedure for purposes of comparison is different from an exact definition, which is probably not a useful concept in the case of asphaltene.

X-ray and neutron scattering techniques have demonstrated that the extent of aggregation of asphaltene can vary in response to changes in temperature, pressure, and solvent quality (Espinat and Ravey, 1993; Carnahan *et al.*, 1993). In a very good solvent, asphaltene can probably best be described as macromolecules with molecular weights in the range of about 1000 to 3000 daltons (Cimino *et al.*, 1995). In poor solvents, asphaltene aggregates are in the colloidal size range, with molecular weights as high as hundreds of thousands (Speight *et al.*, 1985).

Since the tendency to aggregate is what distinguishes asphaltene from other components of a crude oil, all compounds that have a propensity to form aggregates are included in the designation asphaltene as it is used in this review.

Most studies with asphaltene have used one of two different approaches. Asphaltene can be tested as part of the whole oil, or they can be separated by one of the techniques described above, redissolved in a good solvent and tested at known "concentrations." Although it is unusual to have both types of data for comparison, results of wettability tests using the same crude oil and these two different approaches can be quite different (Buckley *et al.*, 1997b). It is not at all clear that solutions of precipitated asphaltene are equivalent to asphaltene as they occur in their native state.

2 WETTABILITY STUDIES

Some of the most widely used techniques for quantifying the effects of asphaltene on wettability include adsorption isotherms, contact angle measurements on flat surfaces, and imbibition into porous media.

2.1 Adsorption

Adsorption of asphaltene on mineral surfaces has been the subject of many studies, as summarized in Table 1. Both monolayer and multilayer adsorption are reported, depending on the solvent and source of asphaltene. Silica, alumina, and various clays rapidly adsorb similar amounts of asphaltene per unit surface area. Water was excluded from most of these tests. When water was present, the amount of material adsorbed decreased (Collins and Melrose, 1983). The net adsorption reported by Curtis (1992) is the result of a sequence of adsorption (from toluene solutions of asphaltene rather than asphaltene) onto a variety of dry surfaces, followed by desorption in water. In contrast to all the studies that focus on dry conditions, net adsorption varies more with the mineral substrate than it does for different asphaltene.

Because water is always present in oil reservoirs, its effect on adsorption is an important aspect of interactions between asphaltene and rock. However, the effects of water have been largely neglected in asphaltene adsorption studies. While it is clear from the work summarized in Table 1 that asphaltene can adsorb on many common mineral surfaces, the extent of their effect in an oil reservoir cannot be deduced from these studies. Whether multilayer adsorption equates to formation damage by asphaltene, as suggested by Acevedo *et al.* (1995), is an interesting question that needs additional study under conditions that include the effects of brine.

2.2 Contact Angle Measurement

On ideal surfaces, contact angles of partially wetting fluids reflect surface energetics. Anything less ideal than brine and oil in the pore spaces of a rock is hard to imagine. Nevertheless, there is a great deal to be learned from properly designed contact angle experiments (Anderson, 1986; Morrow, 1991; Buckley, 1996a).

TABLE 1
Summary of adsorption studies

Reference	Adsorption from	Adsorbed on	Observations
Clementz (1976, 1977)	Asphaltenes (and resins) from propane precipitation of Arabian crude residuum	Dry clays (illite, montmorillinite, and kaolinite) and Berea sandstone	Rapid, strong interactions. Factors influencing adsorption include exchangeable cations, solvent, and nitrogen compounds. Clays stabilized when subsequently exposed to water.
Fritschy and Papirer (1978)	Bitumen dissolved in CS ₂ and <i>n</i> -heptane asphaltenes	Dry silica and alumina (acidic); MgO (basic); ZnO and TiO ₂ (semiconductors) and kaolin	Fast, multilayer adsorption of bitumen in CS ₂ on silica. Asphaltenes in CCl ₄ fit Langmuir monolayer. Similar amounts on the basis of surface area are adsorbed on silica, alumina, and kaolin. Little or no adsorption on basic and semiconductor surfaces.
Czarnecka and Gillott (1980)	Athabasca bitumen and <i>n</i> -pentane asphaltenes	Dry clay minerals isolated from bitumen and Na ⁺ and Ca ²⁺ forms of montmorillinite, illite, chlorite, and kaolinite	<i>IR</i> spectra. More asphaltene adsorbs on Ca ²⁺ forms and less on preheated, drier clays.
Collins and Melrose (1983)	Toluene solution of asphaltene from a light oil reservoir deposit in Alberta	Dry clays and Berea sandstone	Langmuir adsorption isotherms. The presence of water (in toluene or on clay) reduces adsorption.
Dubey and Waxman (1989)	<i>n</i> -pentane insolubles from a tar sand	Dry clays, silicacarbonate	Monolayer adsorption from nonpolar solvents; multilayer from nitrobenzene solutions.
Curtis (1992)	Asphalts dissolved in toluene; desorption under water	Dry granite, limestone, gravels, sandstone, greywacke and basalt	Significant differences in net adsorption depend most on the rock material.
González <i>et al.</i> (1991, 1993, 1994)	Asphaltenes or resins	Dry quartz, calcite, feldspar, and clays	Multilayer adsorption of materials from shale oils, otherwise monolayer adsorption, fit by Langmuir isotherms. More asphaltene than resins adsorb on all materials. Amounts per unit surface area are similar for all materials.
Acevedo <i>et al.</i> (1995)	Toluene solutions of extracted <i>n</i> -heptane asphaltenes from Cerro Negro, Ceuta, and Furrial oils	Dry SiO ₂ scale and heated Ceuta asphaltenes	Cerro Negro (not a troublesome oil) gives monolayer adsorption. Ceuta and Furrial (both problem oils) give multilayer adsorption. Inorganic material serves as nucleus for flocculation.

Most of the contact angles studies reported in the literature can be divided into one of two groups:

- contact angles measured between crude oil and brine, and
- contact angles measured with probe fluids on oil- or asphaltene-treated surfaces.

While measurements of the second type may seem an indirect way of addressing the problem, they are designed to avoid some of the difficulties encountered when measuring contact angles directly with crude oils (e.g., Treiber *et al.*, 1972; Hjelmeland and Larrando, 1986). The second group includes experiments with fluid pairs including glycerol/air (Glotin *et al.*, 1992; Akhlaq *et al.*, 1996) and decane/water (Buckley and Morrow, 1992; Liu and Buckley, 1997) as probe fluids.

Both brine/crude oil and water/decane contact angles show significant hysteresis between water-advancing and water-receding conditions. Water-advancing angles, relevant to displacement of oil by waterflood, are especially difficult to resolve in measurements with crude oil because of pinning of the three-phase line of contact. Direct comparisons of contact angles on treated surfaces show significant differences between crude oils and their asphaltenes in toluene, and even between asphaltenes separated with heptane from a single oil, when the extent of washing was varied (Buckley *et al.*, 1997b). All of these water/oil measurements necessarily include some effects of water. Brine equilibration prior to exposure to oil, is an important part of the experimental design that allows exploration of the effects of brine composition on crude oil/brine/solid interactions.

2.3 Spontaneous Imbibition

In porous media, wetting conditions are often inferred from spontaneous imbibition of either water or oil, or both. Rates and amounts of imbibition have both been used, as in the test proposed by Amott (1959) which compares the change in fluid saturations attributable to spontaneous imbibition to that achieved by spontaneous plus forced displacement. An Amott index to water (I_w) of 1 indicates water-wet conditions, whereas 0 indicates that no water imbibes spontaneously. Often the index to oil (I_o) is subtracted from I_w to give a single wettability index (WI) that can range from -1 (strongly oil-wet) to $+1$ (strongly water-wet) (Cuiec, 1991).

Using WI as a measure of wettability, Cuiec (1986) reported the effects on wettability for several outcrop sandstones contacted with an oil and its vacuum fractions. As shown in Table 2, the oil made cores weakly water wet ($WI = 0.39$) whereas the heaviest fractions—including the 600-700°C fraction with the highest concentration of resins and the 700+°C fraction that contained all the measurable asphaltenes—had little or no effect on wetting. Although there is material in this oil that is capable of altering wetting and the polar resins and asphaltene fractions are the most likely contributors of wettability altering components, there is something different about those components in the more concentrated vacuum distilled fractions compared to their condition in the oil. Conversely, in some of the lighter fractions, even though there are fewer polar components, their effect is enhanced. Results such as these point to the concentration of asphaltenes as being less important than the composition of the oil phase in which they are suspended.

TABLE 2

Wettability index and SARA analysis for a crude oil and its fractions in Fontainebleau sandstone (from Cuiec, 1986)

Fraction	WI	Saturates	Aromatics	Resins	Asphaltenes
Crude oil	0.39	25.9	44.8	6.9	10.6
Toluene	1.00				
210-350°C	0.67	69.6	28.5	1.9	0.0
350-400°C	-0.15	48.9	46.9	4.2	0.0
400-500°C	0.58	38.3	52.8	8.9	0.0
500-600°C	0.06	26.8	61.1	12.1	0.0
600-700°C	0.76	15.2	60.8	24.0	0.0
700+°C	1.00	2.0	54.0	4.0	40.0

3 MECHANISMS OF WETTING ALTERATION

Asphaltene and other crude oil components can alter the wetting of high energy mineral surfaces by several different mechanisms, summarized in Table 3 (Buckley *et al.*, 1998b). Many of the controversies and apparent inconsistencies in the literature regarding the effects of asphaltene on wetting can be explained by these mechanisms of interaction.

The first of these, polar interactions between crude oil components and solid mineral surfaces that occur in the absence of water, is not very specific. Contact angles show that wetting is altered to neutral conditions both by exposure to oil and to asphaltene separated

TABLE 3
Mechanisms of wetting alteration

Interactions	Occur when	Wetting conditions established
Polar	Water is absent	Intermediate or neutral wetting
Ionic	Water is present	<i>Stable water films</i> : surfaces can remain water-wet
		<i>Unstable water films</i> : adsorption by acid/base and ion binding interactions can create a wide range of wetting conditions
Colloidal	Near the onset of asphaltene precipitation	Surfaces become more oil-wet

from oil (Fig. 1). These are the interactions that likely dominate most of the adsorption isotherms reported in the literature.

Of more significance in oil reservoirs are the two remaining categories of interactions. The wetting outcome of ionic interactions depends on the compositions of oil, brine, and solid surface, as well as on temperature and aging time. The influence of brine composition on wetting alteration by A-93 crude oil on glass surfaces exposed first to brine, then to the crude oil is demonstrated in Figure 2. In this case water-

advancing contact angles range from fairly oil-wet ($>150^\circ$) to almost water-wet ($<20^\circ$), depending mainly on brine pH. Ionic interactions in the presence of divalent and multivalent ions in solution can be very oil specific. Some guidance regarding the ability of a particular oil to alter wetting by ionic interactions is provided by acid and base numbers (Buckley *et al.*, 1998b). In general, oils with either high acid number or high base number, but not both, appear to be most active in altering wetting by ionic interactions.

The effect of the colloidal mechanism on wetting alteration by surface precipitation of asphaltenes is evident in Figure 3. If brine and oil treated surfaces are rinsed with an asphaltene precipitant such as decane, instead of an asphaltene solvent such as toluene, a very oil-wet surface results.

Assuming there are asphaltenes present, the contribution of the colloidal mechanism to overall wetting change depends on the solvent quality of the oil with respect to its aggregating fraction (Buckley *et al.*, 1998a). Because asphaltenes can participate in both ionic and colloidal wettability altering mechanisms, the question arises as to which is dominant in a particular situation. For a given oil, that can vary depending on its solvent quality; a simple measure of solvent quality is therefore needed.

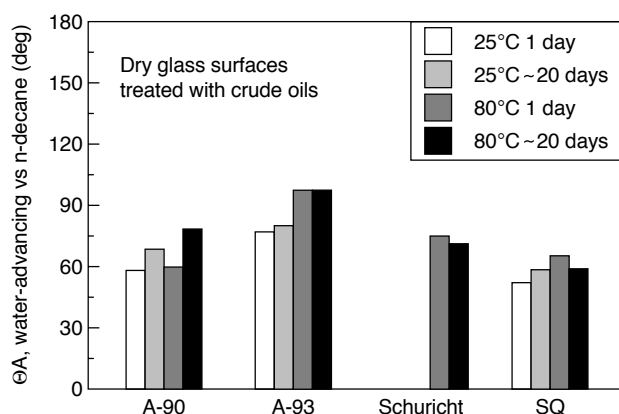


Figure 1

Polar interactions on dry surfaces are illustrated by contact angles on glass surfaces aged in one of four different crude oils. Intermediate wetting conditions are characteristic of interactions between oil components and solid surfaces in the absence of water, with little influence of either temperature or aging time (after Buckley *et al.*, 1998b).

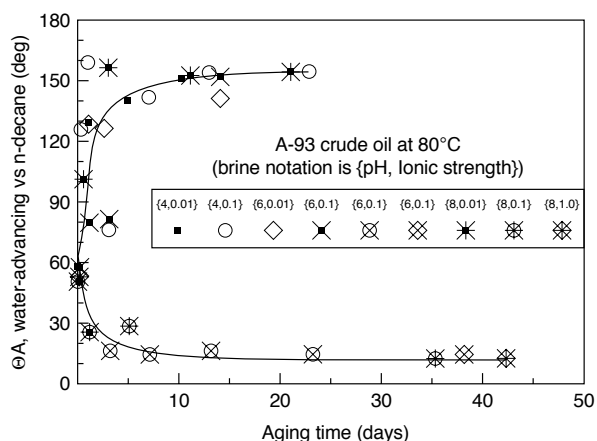


Figure 2

Ionic interactions that dominate in the presence of water are illustrated by contact angles measured on glass surfaces that have been aged in a crude oil from Prudhoe Bay. Brine composition, which influences water film stability, plays an important role in the wetting established. It is typical for changes in wetting to occur slowly and to vary with temperature (after Buckley *et al.*, 1998b).

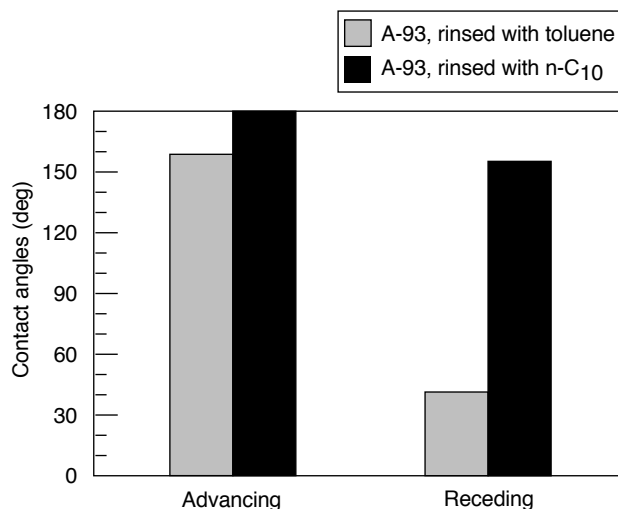


Figure 3

Wetting alteration by both ionic and colloidal mechanisms is illustrated. The high-hysteresis surface observed after toluene washing is principally the result of ionic interactions. Surface precipitation of asphaltenes when the surface is washed with decane makes the surface oil-wet.

4 ASPHALTENE STABILITY AND MIXTURE REFRACTIVE INDEX

Density or API gravity of an oil gives an indication of the relative ability of that oil to disperse its asphaltenes (Buckley *et al.*, 1998a). Higher API gravity (lower density) oils are less able to disperse asphaltenes than are low gravity (high density) oils. Another, more rigorous, measure is refractive index (RI). A schematic diagram is shown in Figure 4 to illustrate the RI of mixtures of a crude oil with an alkane that in sufficient quantity causes asphaltenes to separate from the oil.

In an oil or solvent with high RI , asphaltenes are large molecules or small aggregates. Their influence on wettability is through molecular mechanisms such as the polar and ionic interactions described previously. If the oil is mixed with a low RI precipitant, for example n -pentane or n -heptane, the resulting mixture RI is decreased by an amount that is linearly related to the volume fractions of the mixture components, as indicated by the dashed line connecting 100% oil to 100% alkane. At an RI that is characteristic for a given oil and precipitant, the onset of asphaltene separation can be observed. That RI is indicated in Figure 4 as a

narrow band around the value P_{RI} , which is independent of oil—and therefore asphaltene—concentration. Evidence for concentration independence was shown by mixing oil in varying volume fractions with toluene or α -methyl-naphthalene before beginning the titration. For a wide range of volume fractions, the onset of precipitation was observed at a constant value of RI (Buckley, 1996b).

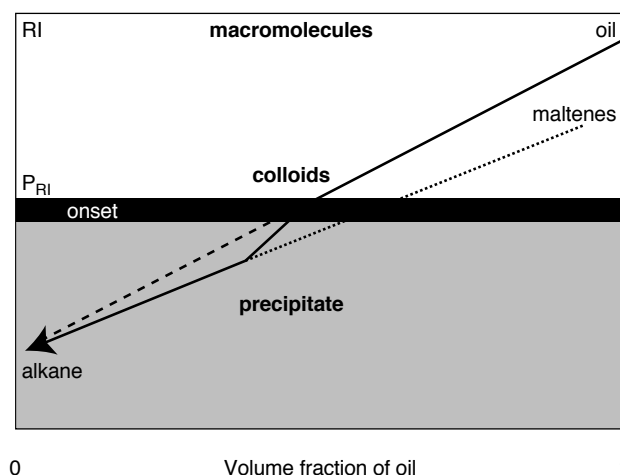


Figure 4

RI of a mixture is a linear function of volume fractions of the mixture components and their individual refractive indices. For mixtures of oil and an alkane, asphaltenes begin to separate at a characteristic value of RI (P_{RI}). Above P_{RI} , mixtures fall on the line between oil and alkane RI s; below it, mixtures fall on the line between alkane and maltenes (oil with the asphaltenes removed), as indicated by the arrow. General regions designating the state of asphaltenes as macromolecular, colloidal, or precipitate are indicated as a function mixture RI .

5 CHANGES IN WETTABILITY AS A FUNCTION OF RI

The results of wettability tests using an oil sample from Prudhoe Bay, diluted with precipitants and solvents, are shown in Figure 5. Details of the experimental method have been published previously (Liu and Buckley, 1997; Buckley *et al.*, 1997). Using the precipitant isooctane, mixtures of 40% oil and 60% precipitant were prepared in which no separated asphaltenes were observed. The downward arrows are used to indicate those mixtures in which asphaltenes appeared. Toluene and α -methyl-naphthalene mixtures were prepared with the same volume fraction, but

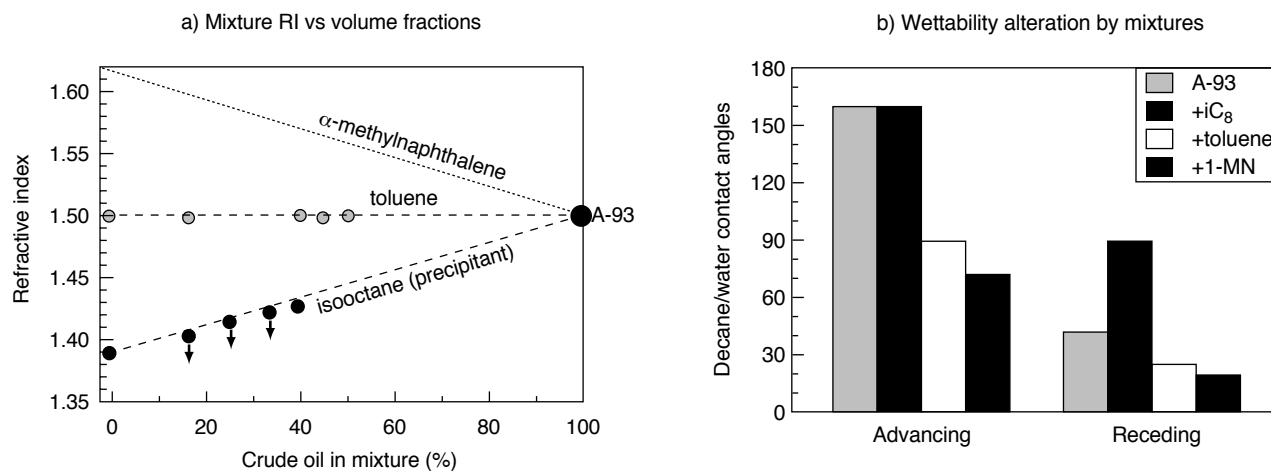


Figure 5

Wettability alteration by crude oil mixtures with solvents and a precipitant:

- a) *RI* of mixtures of A-93 crude oil with isooctane, toluene, and α -methylnaphthalene, and
 b) results measured with water advancing over decane covered surfaces (Buckley *et al.*, 1997).

higher *RI*. The values of *RI* are shown in Figure 5a and the contact angles that result from exposure of glass slides first to synthetic reservoir brine, then to oil or one of the three mixtures are shown in Figure 5b. Since the oil is a good solvent for its asphaltenes, the high advancing angle can likely be attributed at least in part to ionic interactions. Diluting the oil with isooctane produced a similarly high advancing angle and a significant increase in the receding angle, whereas mixtures with the solvents reduced both advancing and receding angles.

6 SURFACE vs BULK PRECIPITATION

None of the mixtures used to treat glass surfaces shown in Figure 5 had any precipitated asphaltene. In general it appears that at least some of the influence of the colloidal surface precipitation occurs before the onset of asphaltene precipitation in bulk (Buckley 1995).

Although quantitative description is difficult for the asphaltene system, related interfacial phenomena have been reported for simpler colloidal dispersions. Williams and Berg (1992) observed that colloidal aggregation of latex particles occurs at an air/water interface under conditions that are stable with respect to aggregation of the same material in the bulk aqueous phase. Picard (1997) varied aqueous phase pH to grow

two-dimensional crystals of colloidal particles at an air/water interface. Crystals formed at the interface only within a narrow range of dispersion stability, when the dispersion was barely stable in bulk.

Translating air/water observations to asphaltenes at oil/water, oil/solid, or water/solid interfaces is far from straightforward. The van der Waals and double layer forces responsible for dispersion of the spherical colloidal particles in the air/water system are fairly well understood and described mathematically. Calculations of DLVO forces at and away from the interface have been made (Williams and Berg, 1992) that predict instability at the interface for conditions that are stable in bulk, depending on the degree of immersion of particles in the aqueous phase.

No such clear-cut model of the dispersion of asphaltenes in an oleic phase has yet emerged. Additional questions arise regarding the shape, size, and chemical variability of asphaltenes. Calculation of the net interfacial forces between asphaltenes at an oil/water interface is not yet possible. Nevertheless, it is reasonable to expect that they will vary from the forces in bulk, perhaps to an even greater extent than is found with air/water colloidal dispersions. What this means with respect to the effect of asphaltenes on wetting is that there may well be a range of marginally stable solvent conditions where the colloidal mechanism of interaction between asphaltenes and solid surfaces is optimized.

7 WETTABILITY ALTERATION IN POROUS MEDIA

Understanding that asphaltenes can influence wetting by more than one mechanism helps to explain some reports in the literature, even though complete descriptions of the oils involved—i.e., acid number, base number, and gravity or *RI*—are usually not available. In the study presented in Table 2 (Cuiec, 1986), it appears that the greatest effect of asphaltenes is evident when the solvent quality is poor, as it is in the lower boiling fractions.

Wolcott *et al.* (1993) compared the effects of various core treatments on both wetting alteration and the amount of organic material deposited. They reported a poor correlation between these two phenomena. Wetting could be altered significantly, especially in the presence of brine, without appreciable organic deposition. Upon exposure to crude oil, wet cores experienced greater alteration of wetting than did dry cores. In dry cores, adding CO₂ to Brookhaven oil increased the amount of material deposited and decreased I_w , consistent with the oil becoming a poorer asphaltene solvent. In wet cores, the effects of adding CO₂ to the oil were much less noticeable.

Redissolved asphaltenes have been shown to alter wetting of Berea sandstone cores (Yan *et al.*, 1997). Mixing of the asphaltene in toluene solution with Soltrol 220 (a mixture of branched paraffins that can precipitate asphaltenes) may have increased colloidal interactions, although differences in imbibition rate that depended on brine composition indicated the importance of ionic interactions as well.

Addition of alkanes ranging from pentane to decane and of varying amounts of hexane to a sample of Prudhoe Bay crude oil suppressed the rate of water imbibition into Berea sandstone cores, consistent with less water-wet conditions generated by the oil as it becomes a poorer solvent (Tang and Morrow, 1996). In these tests, the amounts of added alkane were small and the oil was not particularly close to the onset of precipitation.

Wettability tests under controlled conditions of acid number, base number, and solvent quality are needed to confirm the extent to which wetting alteration can be correlated to these indicators of ionic and colloidal interactions.

CONCLUSIONS

While asphaltenes are certainly implicated in alteration of wetting of high energy surfaces that have been in contact with crude oil, their role is complex. Confusion is exacerbated by lack of agreement about the definition of asphaltenes. For the present discussion, the term asphaltene is used in a very general sense to include any of the high molecular weight, aromatic, and somewhat polar components that form aggregates in response to changes in their oil environment.

Adsorption studies that usually examine the interactions between redissolved asphaltenes and dry mineral powders may fail to capture the fluid/solid interactions that are relevant in a reservoir for several reasons. In the absence of water, the mechanism of adsorption is different from that which would be expected if water were present. Further, asphaltenes that have been separated and redissolved do not necessarily behave as they would in their native crude oil environment.

Two categories of interaction mechanism can contribute to wetting alteration by asphaltenes in a reservoir rock. Ionic interactions depend on the composition of the aqueous phase in addition to the composition of surface active material in the oil and the surface properties of the rock. Asphaltenes in the same oil can be shown to produce very oil-wet or very water-wet conditions by varying the composition of the brine phase. These intermolecular interactions compete with a colloidal interaction mechanism by which asphaltene aggregates can make surfaces oil-wet. The colloidal mechanism is most effective near the onset of asphaltene precipitation.

REFERENCES

- Acevedo S., Ranaudo M.A., Escobar G., Gutiérrez L. and Ortega P. (1995) Adsorption of asphaltenes and resins on organic and inorganic substrates and their correlation with precipitation problems in production well tubing. *Fuel*, 74, 595-598.
- Akhlaq M.S., Kessel D. and Dornow W. (1996) Separation and chemical characterization of wetting crude oil compounds. *J. Colloid Interface Sci.*, 180, 309-314.
- Amott E. (1959) Observations relating to the wettability of porous rock. *Trans., AIME*, 216, 156-162.
- Anderson W.G. (1986) Wettability literature survey. Part 2: Wettability measurement. *JPT* (Nov. 1986) 38, 12, 1246-1262.
- ASTM D2007-80 (1980) Standard test method for characteristic groups in rubber extender and processing oils by the clay-gel adsorption chromatographic method. *ASTM*.

- Buckley J.S. (1995) Asphaltene precipitation and crude oil wetting. *SPE Adv. Tech. Ser.* (Mar. 1995) 3, 1, 53-59.
- Buckley J.S. (1996a) Mechanisms and consequences of wettability alteration by crude oils. *PhD Thesis*, Heriot-Watt University, Edinburgh, Scotland.
- Buckley J.S. (1996b) Microscopic investigation of the onset of asphaltene precipitation. *Fuel Sci. & Tech. Internat.*, 14, 55-74.
- Buckley J.S., Hirasaki G.J., Liu Y., Von Drasek S., Wang J.X. and Gill B.S. (1998a) Asphaltene precipitation and solvent properties of crude oils. *Petroleum Sci. & Tech.*, 16, 3 & 4, 251-285.
- Buckley J.S., Liu Y. and Monsterleet S. (1998b) Mechanisms of wetting alteration by crude oils. *SPEJ*, March 1998, 54-61.
- Buckley J.S., Liu Y., Xie X. and Morrow N.R. (1997) Asphaltenes and crude oil wetting. The effect of oil composition. *SPEJ* (June, 1997) 107-119.
- Buckley J.S. and Morrow N.R. (1992) An overview of crude oil adhesion phenomena. In *Physical Chemistry of Colloids and Interfaces in Oil Production*, H. Toulhoat and J. Lecourtier (eds.). Éditions Technip, Paris, 39-45.
- Carnahan N.F., Quintero L., Pfund D.M., Fulton J.L., Smith R.D. Capel M. and Leontaritis K. (1993) A small angle X-ray scattering study of the effect of pressure on the aggregation of asphaltene fractions in petroleum fluids under near-critical solvent conditions. *Langmuir*, 9, 8, 2035-2044.
- Cimino R., Corra S., Del Bianco A. and Lockhart T.P. (1995) Solubility and phase behavior of asphaltenes in hydrocarbon media. *Asphaltenes: Fundamentals and Applications*, E.Y. Sheu and O.C. Mullins (eds.) NY, Plenum Press, 97-130.
- Clementz D.M. (1976) Interaction of petroleum heavy ends with montmorillonite. *Clays and Clay Minerals*, 24, 312-319.
- Clementz D.M. (1977) Clay stabilization in sandstones through adsorption of petroleum heavy ends. *JPT* (Sept. 1977) 1061-1066.
- Collins S.H. and Melrose J.C. (1983) Adsorption of asphaltenes and water on reservoir rock minerals. Paper SPE 11800 presented at the 1983 *International Symposium on Oilfield and Geothermal Chemistry*, Denver, June 1-3.
- Cuiec L. (1986) Wettability and rock/crude-oil component interactions. Paper presented at the *21st Intersociety Energy Conversion Engineering Conference*, San Diego, Aug. 25-29.
- Cuiec L. (1991) Evaluation of reservoir wettability and its effects on oil recovery. In *Interfacial Phenomena in Oil Recovery*, N.R. Morrow (ed.). Marcel Dekker, Inc., New York City, 319-375.
- Curtis C.W. (1992) Investigation of asphalt-aggregate interactions in asphalt pavements. Preprint, *ACS, Div. Fuel Chem.*, 37, 3, 1292-1298.
- Czarnecka E. and Gillott J.E. (1980) Formation and characterization of clay complexes with bitumen from Athabasca oil sand. *Clay and Clay Minerals*, 28, 3, 197-203.
- Dubey S.T. and Waxman M.H. (1991) Asphaltene adsorption and desorption from mineral surfaces. *SPEJ* (Aug. 1991) 389-395.
- Espinat D. and Ravey J.C. (1993) Colloidal structure of asphaltene solutions and heavy-oil fractions studied by small-angle neutron and X-ray scattering. Paper SPE 25187 presented at the *1993 SPE International Symposium on Oilfield Chemistry*, New Orleans, March 2-5.
- Fritschy G. and Papirer E. (1978) Interactions between a bitumen, its components and model fillers. *Fuel*, 57, 701-704.
- Gloton M.P., Turmine M., Mayaffre A., Letellier P. and Toulhoat H. (1992) Study of asphaltenes adsorption on mineral surfaces by contact angle measurements: kinetics of wettability changes. *Physical Chemistry of Colloids and Interfaces in Oil Production*, H. Toulhoat and J. Lecourtier (eds.) Paris, 89-96.
- González G. and Moreira M.B.C. (1991) The wettability of mineral surfaces containing adsorbed asphaltenes. *Colloids and Surfaces*, 58, 293-302.
- González G. and Moreira M.B.C. (1994) Adsorption of asphaltenes and resins on various minerals. *Asphalt and Asphaltenes*, T.F. Yen (ed.) Elsevier, 219.
- González G. and Travalloni-Louvisse A.M. (1993) Adsorption of asphaltenes and its effect on oil production. *SPEPF* (May 1993) 91-96.
- Hjelmeland O. and Larrondo L.E. (1986) Experimental investigation of the effects of temperature, pressure, and crude oil composition on interfacial properties. *SPEJ* (July 1986) 321-328.
- Liu Y. and Buckley J.S. (1997) Evolution of wetting alteration by adsorption from crude oil. *SPEFE* (Mar. 1997) 5-11.
- Long R.B. (1981) The concept of asphaltenes. *Chemistry of Asphaltenes*, J.W. Bunger and N.C. Li (eds.) ACS, Washington, DC 17-27.
- Morrow N.R. (1990) Wettability and its effect on oil recovery. *JPT* (Dec. 1990) 1476-1484.
- Picard G. (1997) Fine particle 2D crystals prepared by the dynamic thin laminar flow method. *Langmuir*, 13, 3226-3234.
- Speight J.G., Wernick D.L., Gould K.A., Overfield R.E., Rao B.M.L. and Savage D.W. (1985) Molecular weight and association of asphaltenes: a critical review. *Revue de l'Institut français du pétrole*, 40, 1, 51-61.
- Tang G.Q. and Morrow N.R. (1996) Effect of temperature, salinity and oil composition on wetting behavior and oil recovery by waterflooding. Paper SPE 36680 presented at the 1996 *ATCE*, Denver, 6-9 Oct.
- Treiber L.E., Archer D.L. and Owens W.W. (1972) A laboratory evaluation of the wettability of fifty oil-producing reservoirs. *SPEJ* (Dec. 1972) 531-540.
- Williams D.F. and Berg J.C. (1992) The aggregation of colloidal particles at the air-water interface. *J. Colloid and Interface Sci.*, 152, 218-229.
- Wolcott J.M., Groves F.R. Jr., Trujillo D.E. and Lee H.G. (1993) Investigation of crude-oil/mineral interactions: Factors influencing wettability alteration. *SPE Adv. Tech. Ser.*, 1, 1, 117-126.
- Yan J., Plancher H. and Morrow N.R. (1997) Wettability changes induced by adsorption of asphaltenes. *SPEPF*, Nov. 1997, 259-266.

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