Asphaltenes, Water Films, and Wettability Reversal

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We present a transport model for asphaltene diffusion from an oil/water interface through a water film followed by adsorption at a solid/water interface. Using a Langmuir adsorption isotherm, the effects of asphaltene aqueous solubility and adsorption constant K on equilibration time are established. For K greater than 1 nm and for asphaltene solubilities down to 0.1 ppb, adsorption equilibrium, taken to be 1 mg/m^2, occurs within a few hours. Negligible asphaltene solubility does not explain why a water film prevents asphaltene adsorption and wettability alteration in reservoir rock.

Introduction

One of the fundamental pieces of information required for efficient design of oil recovery processes is the reservoir wettability, loosely defined as the preferential affinity of the solid matrix for either the aqueous or oil phases. Current wettability research is aimed at envisioning and understanding reservoir wettability and its development, and varies from microscopic to reservoir scales[1-6]. Underlying this work are three basic assumptions that are now widely accepted as near fact. The first and most significant of these was discovered by Salathiel in his landmark 1972 study[7]. Counter to previous opinion of universal water-wet reservoirs , Salathiel hypothesized a mixed-wet condition with large pores being oil-wet and smaller pores being water-wet, and with the oil-wet and water-wet regions continuously connected. As shown by his core-flood experiments, mixed-wet rock exhibits very low residual oil saturations but slow oil production rates at these low saturations. The second assumption, consistent with Salathiel's vision of continuous oil and water phases, is that configurations of oil in pores involve either direct contact between oil and rock, or separation of the oil phase from the solid by aqueous films, as illustrated in **Fig. 1**. Existence of such water films was first postulated for Athabasca tar sands in the 1930's[8], and since then much has been done to both visualize[6] and describe[9,10] them. The third basic assumption is that in a given pore, when a critical capillary pressure is exceeded, water films destabilize and rupture to an adsorbed molecular film of up to several water monolayers. Crude oil now contacts rock directly, allowing polar oil species to adsorb and/or deposit onto the rock. It is this process that locally reverses the wettability of the rock from water-wet to oil-wet[4,11]. Specifically, asphaltenes, a group of oil components defined by their solubility behavior, are envisioned to be responsible for the wettability alteration because of their polar functional groups which may interact with mineral oxide surfaces. The role of the water films is thus absolutely essential: the presence of a thick water film between the crude oil and the rock surface prevents contact of asphaltenes with the rock and accordingly protects against wettability reversal[10].

Evidence is diverse for the strong role of asphaltenes in influencing reservoir wettability. In imbibition tests of sandstone and limestone cores treated with different oil fractions, oil-wet cores are produced only by the heaviest fraction, the residue[12], which contains the asphaltenes. In Salathiel's experiments[7], asphaltic oil produced mixed-wet cores. More recent experiments show strong adsorption of asphaltenes from organic solutions onto clays and sandstones, causing dramatic wettability shifts[13,14]. Finally, upon contacting deasphalted crude oil with smooth glass surfaces, Buckley and Morrow found no wettability alteration, as contrasted with strong wettability alteration caused by the original oil[1]. These results contribute to the belief that asphaltenes cause reservoir mixed wettability.

Much is still unknown about the mechanism of wettability alteration. The accepted explanation of the water film's protective role is that the virtual insolubility of asphaltenes in water precludes their transport to the rock surfaces. (Otherwise, initially water-wet reservoirs should eventually become completely oil-wet upon initial migration and invasion of asphaltic crude oil.) Over geologic time, however, even a minuscule water solubility of asphaltenes may permit diffusion through a water layer and adsorption at the rock surface. Unfortunately, experimental study of this adsorption process is hindered by the chameleon-like behavior of asphaltenes: their structure strongly depends on solvent characteristics.

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Asphaltenes are known to be large, heterocyclic, aromatic compounds with nitrogen, oxygen, and sulfur atoms throughout the ring structure[15]. They are by definition insoluble in small alkanes, but soluble to different

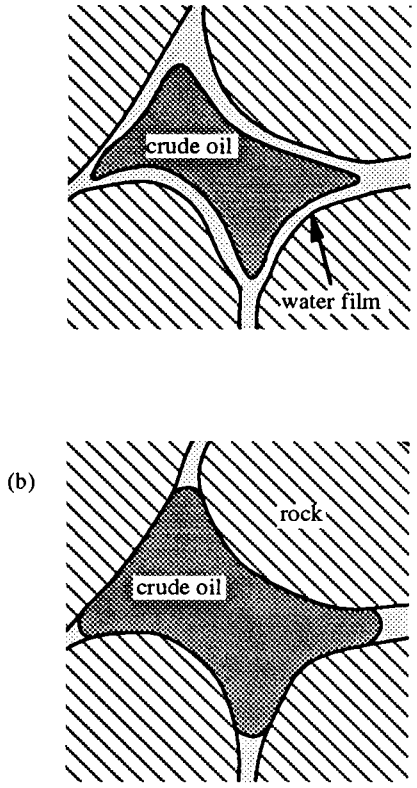

Fig. 1–Schematic of a pore cross-section in a porous medium. Flow is into the plane of the paper. (a) Water-wet rock grains are surrounded by a thin film of brine and are not contacted by oil. (b) Mixed-wet pore has adjacent oil-wet and water-wet regions.

degrees in aromatic solvents. In crude oil, asphaltenes are believed to exist as aggregates of various sizes stabilized by an outer coating of amphiphilic resin molecules, which contain a polar end directed toward the asphaltenes, and a nonpolar aliphatic end which allows for solubility in the crude oil[13,14,16-19]. Adsorption of asphaltenes from organic solutions onto mineral surfaces displays a Langmuir adsorption isotherm and reversible adsorption at low asphaltene concentrations[14,16,17]. Higher concentrations lead to irreversible adsorption, possibly because asphaltene aggregation at the mineral surface makes simultaneous bond breakage, a highly improbable event, necessary for desorption. When crude oil directly contacts a surface in the absence of water, adsorption and wettability alteration occur immediately. The final adsorbed configuration, after exchange of different molecular-weight asphaltenes, may take days or longer to be completed, but results only in qualitatively different wettability[20]. It is dangerous to extrapolate these results to adsorption from an aqueous phase because asphaltene structures in water may only be speculated.

Fig. 2 illustrates potential configurations of asphaltenes and resins at the solid/water and oil/water interfaces and in the bulk oil and water phases. A single asphaltene molecule is drawn as a dark line with a circular patch representing the aromatic sheet with interspersed polar regions. Within the crude oil, asphaltenes can exist as reverse micelles surrounded by resin molecules, which are illustrated by a polar head group and hydrocarbon tail. We indicate these micelles schematically by grouping several asphaltene sheets. Recent

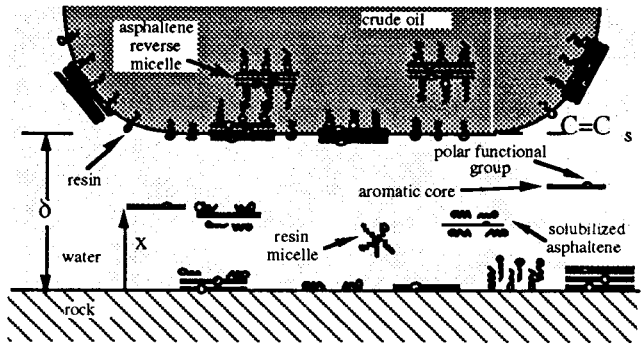

Fig. 2–Diffusion of asphaltenes and/or resins from the oil phase through a thin aqueous film followed by adsorption on the solid matrix.

work[21,22] on water-in-crude oil emulsions suggests that asphaltenes and resins adsorb at the oil/water interface as aggregates of various sizes, depending upon solvent aromaticity and resin-to-asphaltene ratio. At the oil/water interface, the polar asphaltenes presumably lose their outer resin shell when oriented toward the water phase, as shown schematically in **Fig. 2**. It seems unlikely that resin-stabilized hydrophobic asphaltene micelles diffuse through the water phase and adsorb onto the mineral surface. More likely is diffusion of smaller components: single, polar asphaltene molecules; resin molecules, which are likely more soluble than the asphaltene molecules because of their amphiphilicity and their lower molecular weight; hydrophilic resin micelles, with alkyl stabilizing resin molecules oriented toward the core, with or without asphaltenes inside; or some small association of complexed asphaltenes and resins. These possible molecular structures are all displayed in **Fig. 2**. Asphaltenes are shown adsorbed at the rock/water interface with the planar faces toward the solid. Adsorption of asphaltenes probably occurs through polar interactions between the mineral surface and the heteroatoms or pyridinic and carboxylic acid groups of the asphaltenes. Resins may also adsorb through polar interactions, possibly forming bilayers at high enough concentrations. When enough molecules have reached the rock surface, adsorption likely becomes irreversible after rearrangement and aggregation from an initial configuration. We treat the diffusion and adsorption processes in **Fig. 2** as occurring via a single component, denoted generically as an asphaltene molecule. This viewpoint is clearly over-simpli-

fied, but should nevertheless allow an estimate of the expected time scales.

We specifically address the question of whether very low solubilities of asphaltenes in water can indeed prevent diffusion through a water film. The purpose of this paper is to calculate the total time for diffusion of low solubility asphaltenes through a water layer followed by adsorption onto the rock surface. This will in part confirm or deny the validity of the negligible solubility argument to explain the proposed protective role of water films in wettability alteration of reservoirs.

Theory

Diffusion of surface-active species to an interface followed by adsorption is a well-studied problem in the dynamic surface tension literature[23]. The classical results of both Ward and Tordai[24]and Sutherland[25]are similar to the asphaltene-adsorption problem, in that all three demand solution of Fick's law of diffusion. We, however, are interested in diffusion through a finite thickness film initially devoid of the diffusing species, whereas they consider diffusion from a bulk solution, initially at a finite constant concentration which remains fixed infinitely far from the interface.

The problem we address is shown schematically in **Fig. 2**. An oil phase is separated from the rock by a water layer of thickness δ. For connate water saturations typical of reservoir discovery, we take δ to be 100 nm or less, and certainly less than 1 μm. At the oil/water interface, a constant equilibrium aqueous-phase solubility concentration of asphaltenes is assumed. At the solid/aqueous interface, the rate of asphaltene adsorption is identical to the diffusive flux of asphaltenes to the surface. Adsorption density, Γ, follows a simple Langmuir isotherm, and local equilibrium is assumed at the solid/water interface. Because our primary concern is the role of asphaltene diffusion through the water layer, kinetic resistances to sorption at the oil/water or mineral/water interfaces are not considered. Some equilibration of the oil/water interface likely occurs prior to actual oil invasion into water-filled pores and formation of the aqueous films. For the mineral surfaces, we argue that dramatic wettability reversals occur through early contact of oil components with the surface. Subsequent rearrangement of the adsorbed molecules likely contributes secondary wettability effects[20]. Clearly, including finite kinetic resistances increases adsorption time.

Initially, the aqueous phase contains no asphaltenes, after which they diffuse from the oil/water interface and adsorb upon arrival at the solid/water interface. Eventually, the solid surface equilibrates with adsorbed asphaltenes at the aqueous asphaltene solubility limit. Our goal is to investigate the effect of very low asphaltene solubility on the time to reach surface equilibration.

As the concentration of asphaltene species in the oil phase is much greater than their corresponding aqueous solubilities, diffusion resistance in the oil phase plays no role in the overall diffusion process. Accordingly, we consider only one-dimensional asphaltene diffusion through the water layer, which is stated in reduced variables as follows

$$\frac{\partial C(z,\tau)}{\partial \tau} = \frac{\partial^2 C(z,\tau)}{\partial z^2} \tag{1}$$

with boundary conditions of initially zero asphaltene concentration in the water phase and saturation concentration of asphaltenes maintained in the water below the oil/water interface

$$C(z,0) = 0 \tag{2}$$

$$C(1,\tau) = c_s\delta/\Gamma_{max} \equiv C_s. \tag{3}$$

At the solid surface, all the asphaltene that diffuses to the surface adsorbs onto the rock

$$\frac{\partial\theta(\tau)}{\partial\tau} = \left.\frac{\partial C(z,\tau)}{\partial z}\right|_{z=0} \tag{4}$$

and can be described by a Langmuir isotherm

$$\theta(\tau) = \frac{\frac{K}{\delta}C(0,\tau)}{1+\frac{K}{\delta}C(0,\tau)} \tag{5}$$

where $C=c\delta/\Gamma_{max}$, $\theta=\Gamma/\Gamma_{max}$, $z=x/\delta$, $\tau=Dt/\delta^2$, x is the distance from the rock surface, t is time, K is the adsorption equilibrium constant in the Langmuir isotherm, c is the asphaltene aqueous-phase concentration, c_S is the solubility concentration, Γ is the asphaltene adsorption at the solid/water interface, Γ_{max} describes the maximum adsorption, and D is the asphaltene diffusivity in water.

A schematic of a Langmuir isotherm is shown in **Fig. 3**. Langmuir adsorption implies equivalent adsorption sites and maximum monolayer coverage. The isotherm is characterized by two parameters: K and Γ_{max}. K is the slope of the isotherm at the origin and also gauges the thickness of the asphaltene adsorbed layer. Accordingly, the important nondimensional ratio K/δ appears in Eq. (5).

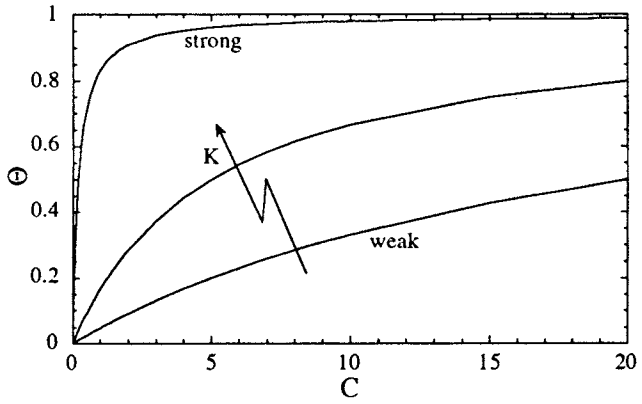

Fig. 3–Schematic of a Langmuir isotherm illustrating strong and weak adsorption.

When K is large, almost all of the adsorption occurs at low concentrations. In essence, every arriving molecule sticks to the surface until maximum coverage is obtained. This leads to almost irreversible adsorption, termed strong

adsorption. Conversely, when K is small, the isotherm appears to be linear for much of the concentration range. Significant concentration is needed to approach maximum adsorption. This regime is termed weak adsorption and is reversible. It is important to note that strong adsorption, in the sense of **Fig. 3**, is not necessarily equivalent to wettability reversal. Simple maximum Langmuir coverage, even at extremely dilute concentrations, may not be enough to alter wettability from highly water-wet to highly oil-wet.

As indicated in Eqs. (1) - (5), the transient asphaltene concentration profile, $C(z,\tau)$, depends upon two dimensionless parameters, K/δ and $C_S = c_S\delta/\Gamma_{max}$. The first of these parameters gives the ratio of the adsorption layer thickness to the diffusion path length, the water film thickness. As described above, a large value of K, and therefore K/δ, implies a high initial slope in the Langmuir isotherm, and therefore strong adsorption at very low aqueous asphaltene concentrations. The second parameter is a capacity factor, indicating the relative asphaltene capacity of the bulk to that of the surface: $c_S\delta/\Gamma_{max} = c_S/\Gamma_{max}a_V$, where a_V is the rock surface area to aqueous film volume ratio. The product of the two parameters, c_SK/Γ_{max}, is the ratio of the solubility concentration to the characteristic concentration at which maximum adsorption is reached, Γ_{max}/K. When this value is high, the solubility concentration occurs well into the horizontal region of the Langmuir isotherm. When this value is low, however, the solubility concentration falls within the linear regime of the Langmuir isotherm. This means that maximum (i.e., monolayer) coverage may never be reached, and greatly limits the possibility for wettability alteration.

The mathematical solution to Eqs. (1) - (5) is outlined in Appendix A. Typical transient concentration profiles, obtained from Eqs. (A-3) and (A-8), are shown in **Fig. 4** for asphaltenes diffusing from the oil/water interface at $z=1$ to and adsorbing on the mineral surface at $z=0$. For the particular parameter values chosen of $K/\delta = c_S\delta/\Gamma_{max} = 1$, the asphaltenes first reach the mineral/water interface at a dimensionless time of about 0.01. Thereafter, adsorption at the mineral surface increases, as does the corresponding aqueous asphaltene concentration, until $C(0,\tau) = C_S$ and equilibrium is attained. Note that the slope of the concentration profile at $z=0$ remains finite as the concentration there builds depicting the finite asphaltene flux and the corresponding increasing adsorption amount as demanded by Eq. (4).

Results and Discussion

We desire the time at which adsorption equilibrium is reached, τ_{eq}, as a function of both K/δ and C_S. τ_{eq} is defined here as the time at which θ reaches the fraction $1-\alpha$ of its maximum attainable value, $\theta(C_S)$, which is in general less than unity. Graphs of τ_{eq} versus K/δ for different values of C_S, and τ_{eq} versus C_S for different values of K/δ are shown on log-log scales in **Figs. 5** and **6**, respectively, with α taken as 0.01 (i.e., for $\Gamma/\Gamma_{eq}=0.99$). **Fig. 5** shows a clear maximum at roughly $K/\delta = C_S^{-1}$. This is the location of the elbow in the adsorption isotherm. For values of $K/\delta < C_S^{-1}$, the Langmuir-isotherm equilibration times (solid lines) approximate those of a linear isotherm, $\theta = (K/\delta)C$. The linear-isotherm solution, shown by the dashed line in **Fig. 5**, is given by Eq. (3.13-9) in Carslaw and Jaeger[26]. By

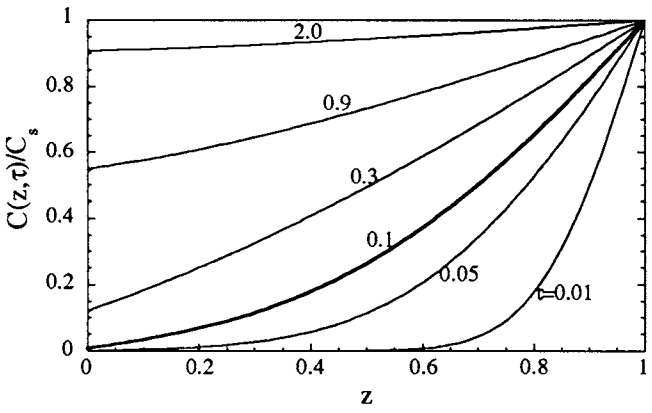

Fig. 4 –Asphaltene concentration profiles in the water film with $K/\delta=1$ and $c_s\delta/\Gamma_{max}=1$.

considering the limits of that equation for both $K/\delta \rightarrow 0$ and $K/\delta \rightarrow \infty$, we establish the following linear relation for the dashed line

$$\tau_{eq} = (\ln \alpha^{-1})\frac{K}{\delta} - \frac{4}{\pi^2}\ln\frac{\pi\alpha}{4} \qquad (6)$$

At large K/δ, the effect of increasing K/δ in the linear-isotherm regime is to increase linearly the amount of adsorption, and therefore the time to reach this increasing equilibrium amount. At very small K/δ, the time to reach equilibrium approaches a constant value dependent on α (i.e., 1.964 in **Fig. 5** where $\alpha=0.01$).

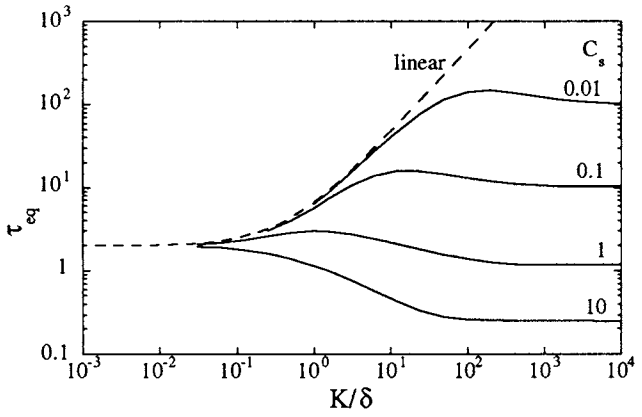

Fig. 5–Adsorption equilibration time as a function of K/δ for varying C_S and for the linear isotherm ($C_S \rightarrow 0$), shown as a dashed line.

For $K/\delta < C_S^{-1}$ in **Fig. 5**, all Langmuir-adsorption equilibrium times approach those of the linear isotherm. This is seen in **Fig. 5** where the solid lines merge into the dashed line. In the second regime of **Fig. 5**, $K/\delta > C_S^{-1}$, equilibration time decreases with increasing K/δ and approaches an asymptotic value that depends on C_S. In the infinite K/δ limit, adsorption at the solid surface saturates to Γ_{max} while the aqueous concentration adjacent to the solid remains essentially zero. The process can be thought of as having two distinct time steps: diffusion and saturation of

adsorption to θ=1, while zero aqueous-phase bulk concentration is maintained at the solid surface, followed by saturation of the bulk film to concentration c_S with a no-flux boundary condition at the solid surface. Only the first time scale is relevant to our definition of τ_{eq}. To find this value of τ_{eq}, Eq. (4) is solved in the following form

$$\theta = \int_0^{\tau} \frac{\partial C}{\partial z}(0,\tau)d\tau = 1-\alpha \qquad \text{for } K/\delta > C_s^{-1} \to \infty \tag{7}$$

where $C(z,\tau)$ is now the solution to Eq. (1) with the solid/water interface boundary condition set to $C(0,\tau)$=0. We find that

$$C_s\left[\tau_{eq} + 2\sum_{n=1}^{\infty}\frac{(-1)^{n+1}}{n^2\pi^2}\left(e^{-n^2\pi^2\tau_{eq}} - 1\right)\right] = 1-\alpha \qquad \text{for } K/\delta > C_S^{-1} \to \infty \tag{8}$$

For large values of τ_{eq}, Eq. (8) reduces to the result

$$\tau_{eq} = (1-\alpha)\, C_S^{-1} \qquad \text{for } K/\delta > C_S^{-1} \to \infty \tag{9}$$

Fig. 5 confirms this behavior for large K/δ. Away from this asymptotic limit, equilibration of the bulk solution and equilibration of the interface occur together, thereby slowing the adsorption process and giving rise to the observed maxima.

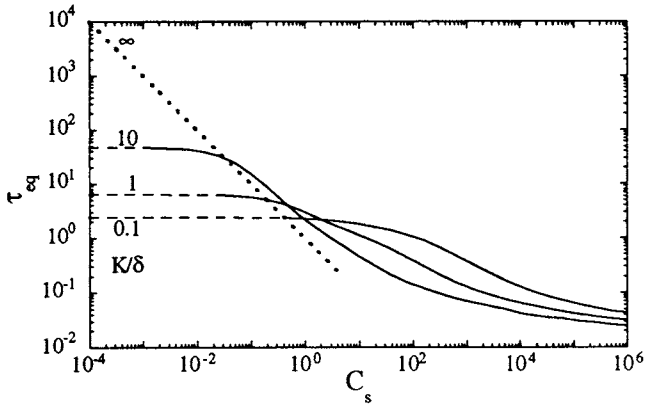

Fig. 6–Adsorption equilibration times as a function of C_S for varying K/δ. Dashed lines correspond to the $C_S \to 0$ limit of a linear isotherm whereas the dotted line corresponds to the $K/\delta > C_S^{-1} \to$ limit of Eq. (9).

The same information can be plotted as τ_{eq} versus C_S, as shown in **Fig. 6**, allowing for examination of a larger range in C_S. This plot shows even more dramatically the effect of asphaltene aqueous solubility. Below a given C_S value, which depends on K/δ, the linear isotherm emerges, with equilibration time independent of solubility and linearly related to K/δ. These curves correspond to the linear-isotherm curve of **Fig. 5** and, therefore, are also shown in **Fig. 6** by dashed lines. In this weak-adsorption limit, the equilibrium adsorption amount scales linearly with C_S and so does the diffusion flux. Thus, τ_{eq}, which is the ratio of these two quantities, becomes independent of C_S, as quantified in Eq. (6).

Included as a dotted line in **Fig. 6** is the infinite K/δ limit, which is valid only for $K/\delta > C_S^{-1}$. In this strong-adsorption limit, equilibrium adsorption equals Γ_{max}, even for infinitesimal values of C_S , while the diffusion flux remains proportional to C_S. Hence, τ_{eq} is now inversely proportional to C_S, as quantified in Eq. (9). Once C_S drops below $(K/\delta)^{-1}$, the equilibrium time approaches a finite value given by the linear-isotherm limit.

Finally, to obtain the infinite solubility asymptote, we consider that adsorption is negligible with respect to the bulk concentration, and therefore that this limit is also approximated by the no-flux boundary condition, but now for τ_{eq} approaching zero. Appendix B demonstrates that

$$erfc\left(\frac{1}{2\sqrt{\tau_{eq}}}\right) = \frac{(1-\alpha)}{2\alpha C_S(K/\delta)} \qquad \text{for } C_S \to \infty \tag{10}$$

where erfc represents the complimentary error function. This limit is attained at $\tau_{eq} \le 0.1$ in **Fig. 6**, but is not displayed.

The most relevant regions in **Fig. 6** are those of the dashed and dotted curves: low solubility with weak adsorption and low solubility with strong adsorption. If adsorption is minimal at low solubilities, then wettability alteration is unlikely due to a lack of adsorbed asphaltene molecules. Conversely, large K/δ allows for maximum surface coverage even with very small solubilities. In this case wettability reversal is more likely. The role of decreasing solubility is clearly demonstrated in **Figs. 5** and **6**: it increases the equilibration time. For weak adsorption the linear-isotherm limit in Eq. (6) emerges, whereas for strong adsorption equilibration time obeys Eq. (9).

For these results to be applied to the asphaltene adsorption problem, parameters must be estimated to describe asphaltene behavior in aqueous solutions. Unfortunately, accurate values of K, Γ_{max}, D, and c_S are difficult to obtain. We choose D and Γ_{max} using Speight's recent review of asphaltene structure[15]. He suggests an average molecular weight of 2000, based on molecular weight determinations in good solvents that do not lead to asphaltene aggregation. A proposed monomolecular asphaltene structure is a hydrocarbon sheet of saturated and unsaturated rings. We estimate a reasonable size of 50 Å diameter and 5 Å thick. To determine D we use a theory for diffusion of oblate ellipsoids with radii 2.5 and 25 Å[27]. To be conservative, we use one order magnitude smaller than predicted by the theory, 10^{-7} cm^2/s. An approximate Γ_{max} value of 5 x 10^{-7} mol/m^2 is calculated for a monolayer of asphaltenes standing on end. A more probable conformation is adsorption with the 50 Å diameter side toward the rock, but again we opt for a conservative estimate by maximizing the adsorption necessary for wettability alteration. Our adopted Γ_{max} value agrees with values found for adsorption from organic solvents onto various mineral oxides[13,14,16,17]. With these two parameters fixed, we consider K ranging from 10^{-9} to 10^{-1} m, and c_S between 0.1 ppb and 10^3 ppm.

Fig. 7 is a plot of dimensional equilibration time versus solubility for an infinite adsorption constant and for K=10^{-9} m . As indicated by the dashed line, the small K value cor-

responds to a linear-adsorption isotherm for which equilibration times are independent of solubility according to Eq. (6). The dotted line provides an upper bound for equilibration time estimation. All finite K values have a corresponding solubility below which equilibration time is independent of solubility. Curves are shown for two water layer thicknesses, 100 nm and 1 μm, the latter presumably being the maximum possible thickness of water films existing within a typical pore. For this entire parameter range, the maximum equilibration time is about 10 hours, clearly accessible on laboratory time scales. Every order of magnitude decrease in diffusivity increases equilibration time by one order of magnitude. Even a few orders of magnitude change in parameters maintains the equilibration time, if not within laboratory time scales, certainly well below geological time scales.

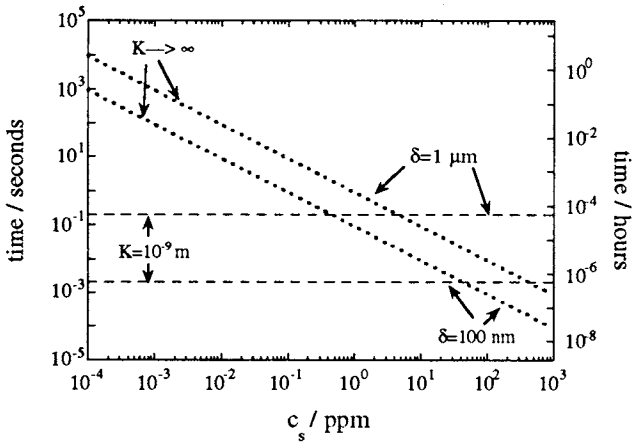

Fig. 7– Adsorption equilibration times as a function of c_S for D=10^{-7} cm^2/s.

Implications

Our results show that for asphaltene species of extremely low solubilities (less than 1 ppb) diffusing through water films of finite thickness (less than 1 μm), equilibrium mineral-surface coverage is reached in a few hours. Adoption of unlikely parameter values still demands rock-surface equilibration within laboratory time scales. One effect of low asphaltene solubility is to limit the number of adsorbed molecules that are present at equilibrium; this obviously prevents wettability alteration. However, it is possible to reach saturation coverage with very low solubilities if there is a high adsorption constant. This condition is represented as the K approaching infinity curve of **Fig. 7** for very low solubilities, given by Eq. (9). Equilibration times are still on the order of a few hours, and saturation coverage to Γ_{max} is expected for large enough K (i.e., for $K/\delta >> C_S^{-1}$).

Our calculations imply that low solubility asphaltenes can diffuse through water films to arrive at rock surfaces in relatively short time scales. Asphaltene molecules are not prevented from arrival at rock surfaces by a protective water film. Thus, if asphaltene adsorption in the presence of water is strong enough to reverse rock wettability, then all asphaltic oil reservoirs should be oil-wet, which is not observed. We speculate that asphaltic species arriving at the rock surface through water do not adsorb enough to alter wettability to oil wetness. Apparently, rupture of the water film followed by direct deposition of the asphaltenic material residing at the oil/water boundary is needed to reverse wettability.

Upon water-film rupture, the degree of wettability alteration presumably depends on the amount and structure of asphaltenes present at the oil/water interface. **Fig. 2** schematically depicts such configurations. As a result of significant asphaltene and resin adsorption, rigid skins may form at crude oil/water interfaces[28-30], especially when asphaltenes are at the point of incipient flocculation in the crude oil[21]. Deposition of such a congealed skin suggests strong, irreversible wettability reversal at the locations of water-film rupture[4]. While there is evidence that increased aggregate size at the oil/water interface enhances the degree of wettability alteration[2], the qualitatively essential feature for wettability reversal appears to be direct contact between oil/water and mineral/water interfaces after water-film rupture. The deposition of a coherent, multilayer, skin-like film is apparently necessary to alter the mineral surface wettability from strongly water-wet to strongly oil-wet (i.e., from a near zero contact angle through the water phase to one significantly greater than 90°).

Conclusions

Calculations have been performed of diffusion times for very low solubility asphaltenes from an oil/water interface through a water film followed by adsorption on a rock surface. Contrary to popular belief, our new results show adsorption equilibration within a few hours, and even for extremely low solubilities, within laboratory time scales. Apparently, asphaltene adsorption on reservoir rock in the presence of a finite water film is not massive enough to initiate significant wettability alteration. We argue that water-film rupture followed by direct deposition of crude oil onto rock is the likely origin of wettability reversal in reservoir rock.

Nomenclature

a_i = coefficients in Eq. (A-6)
a_V = rock surface area to aqueous film volume ratio
c = asphaltene aqueous concentration
C = dimensionless aqueous asphaltene concentration
D= asphaltene diffusivity in water
g = parameter used in computing coefficients in Eq. (A-6)
j = time step index
K = adsorption equilibrium constant
m = time step index
n = summation index
t = time
U = dimensionless concentration with boundary conditions in Eq. (A-2)
V = dimensionless concentration with boundary conditions defined by Eqs. (2) - (4) and (A-2)
x = distance
z = dimensionless distance
α = fraction of surface coverage unadsorbed at equilibrium
Γ = adsorption density

δ = water-film thickness
ζ = dummy integration variable
θ = surface coverage
τ = dimensionless time

Subscripts

o = zero asphaltene adsorption
eq = equilibrium
max = maximum
s = solubility

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Appendix A: Superposition Integral Solution

The solution to Eqs. (1) - (5) is obtained by writing

$$C(z,\tau) = U(z,\tau) + V(z,\tau) \tag{A-1}$$

with boundary conditions on U

$$1.\ U(z,0) = 0$$

$$2.\ U(0,\tau) = 0 \tag{A-2}$$

3. $U(1,\tau) = C_s$

U is easily found to be the series solution

$$U(z,\tau) = C_s\left[z + \frac{2}{\pi}\sum_{n=1}^{\infty}\frac{(-1)^n}{n}\sin(n\pi z)\; e^{-n^2\pi^2\tau} \right] \quad \text{(A-3)}$$

Solving for V is not straightforward because of the time-dependent boundary condition at the solid interface, Eq. (4). $V(z,\tau)$ is, however, amenable to solution by Duhamel's superposition integral[31]

$$V(z,\tau) = \int_0^{\tau} \frac{\partial V(0,\zeta)}{\partial \zeta}\left[(1-z) - \frac{2}{\pi}\sum_{n=1}^{\infty}\frac{1}{n}\sin(n\pi z)\; e^{-n^2\pi^2(\tau-\zeta)} \right] d\zeta \quad \text{(A-4)}$$

In order to find $V(0,\tau)$, the solid/water boundary condition in Eq. (4) is applied, leading to the following result, implicit in $V(0,\tau)$

$$\frac{K}{\delta}\frac{\partial V(0,\tau)}{\partial \tau} = \left\{ C_s\left[1 + 2\sum_{n=1}^{\infty}(-1)^n e^{-n^2\pi^2\tau} \right] - \int_0^{\tau}\left[\frac{\partial V(0,\zeta)}{\partial \zeta} x \left(1 + 2\sum_{n=1}^{\infty} e^{-n^2\pi^2(\tau-\zeta)} \right) \right] d\zeta \right\} x \left[1 + \frac{K}{\delta} V(0,\tau) \right]^2 \quad \text{(A-5)}$$

This equation is solved numerically by discretizing the integral and derivatives over equal sized time steps[32], defined as $j\,\Delta\tau = \tau_{j+1}$, and then solving for $V(0,\tau_{m+1})$ in terms of $V(0,\tau_{j\le m})$. We use a fully implicit scheme: the right side of Eq. (A-5) is evaluated at τ_{m+1} and the derivative as $[V(0,\tau_{m+1})-V(0,\tau_m)]/\Delta\tau$. This yields a cubic equation for each $V(0,\tau_{m+1})$

$$a_3\left[V(0,\tau_{m+1})\right]^3 + a_2\left[V(0,\tau_{m+1})\right]^2 + a_1 V(0,\tau_{m+1}) + a_0 = 0 \quad \text{(A-6)}$$

where

$$a_3 = \Delta\tau + \frac{2}{\pi^2}\sum_{n=1}^{\infty}\frac{1-e^{-n^2\pi^2\Delta\tau}}{n^2}$$

$$a_2\left(V(0,\tau_m)\right) = 2\frac{\delta}{K}a_3 - g\left(V(0,\tau_m)\right)$$

$$a_1\left(V(0,\tau_m)\right) = \frac{\delta}{K}\left[1 + \frac{\delta}{K}a_3 - 2g\left(V(0,\tau_m)\right) \right]$$

$$a_0\left(V(0,\tau_m)\right) = -\frac{\delta}{K}\left[\frac{\delta}{K}g\left(V(0,\tau_m)\right) + V(0,\tau_m) \right]$$

$$g\left(V(0,\tau_m)\right) = C_s\left[\Delta\tau + 2\Delta\tau\sum_{n=1}^{\infty}(-1)^n e^{-n^2\pi^2 m\Delta\tau} \right] + V(0,\tau_{m+1})a_3 - \sum_{j=1}^{m-1}\left\{ \left[V(0,\tau_{j+1}) - V(0,\tau_j) \right] x \left[\Delta\tau + \frac{2}{\pi^2}x \sum_{n=1}^{\infty}\frac{e^{-n^2\pi^2 m\Delta\tau}}{n^2}\left(e^{n^2\pi^2 j\Delta\tau} - e^{n^2\pi^2(j-1)\Delta\tau} \right) \right] \right\} \quad \text{(A-7)}$$

which is solved using the Newton-Raphson method. Typical time increments are $\Delta\tau = 10^{-3}$.

Once Eq. (A-6) is solved at each time step, the full concentration profile, $C(z,\tau)$, may be obtained by discretizing the integral in Eq. (A-4) similar to that in Eq. (A-5)

$$V(z,\tau_{m+1}) = \left[V(0,\tau_{m+1}) - V(0,\tau_m) \right]\left[1 - z - \frac{2}{\Delta\tau\pi^3}x \sum_{n=1}^{\infty}\frac{\sin(n\pi z)}{n^3}\left(1 - e^{-n^2\pi^2\Delta\tau} \right) \right] + \sum_{j=1}^{m-1}\left[V(0,\tau_{j+1}) - V(0,\tau_j) \right]\left[1 - z - \frac{2}{\Delta\tau\pi^3}x \sum_{n=1}^{\infty}\frac{\sin(n\pi z)}{n^3} e^{-n^2\pi^2\tau_{m+1}}\left(e^{n^2\pi^2\tau_{j+1}} - e^{n^2\pi^2\tau_j} \right) \right] \quad \text{(A-8)}$$

followed by addition with Eq. (A-3).

Appendix B: Large Solubility Asymptote

To establish the $C_S \to \infty$ limit, we solve Eqs. (1) - (3) of the text along with the no-flux condition

$$\frac{\partial C(0,\tau)}{\partial z} = 0 \quad \text{(B-1)}$$

using the method of Laplace transforms. While in Laplace space, s, we expand $C(0,s)$ for large s and invert into the time domain giving $C(0,\tau)$ in the limit of small τ. The Langmuir isotherm, Eq. (5), with $\theta = 1-\alpha$ completes the problem to yield Eq. (10) of the text at leading order.

SI Metric Conversion Factors

ft x 3.048* E–01 = m

*Conversion factor is exact

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