Evaluation of Reservoir Wettability and its Effect on Oil Recovery

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Objectives

This project has three main goals. The first is to achieve improved understanding of the surface and interfacial properties of crude oils and their interactions with mineral surfaces. The second goal is to apply the results of surface studies to improved predictions of oil production in laboratory experiments. Finally, we aim to use the results of this research to recommend ways to improve oil recovery by waterflooding.

In order to achieve these goals, the mechanisms of wetting alteration must be explained. We propose a methodology for studying those mechanisms on mineral surfaces, then applying the results to prediction and observation of wetting alteration in porous media. Improved understanding of the underlying mechanisms will show when and how wettability in the reservoir can be altered and under what circumstances that alteration would be beneficial in terms of increased production of oil.

Summary of Technical Progress

1. Crude Oil/Brine/Solid Interactions

Crude oils exhibit a wide range of colloidal stability of their asphaltene fraction. In some, asphaltenes are very close to the onset of precipitation, while in others the asphaltenes are relatively stable. The value of refractive index (RI) of an oil sample and the RI at which

precipitation is first observed are distinctive properties of each crude oil.^{1,2} The difference between these two values is a measure of the stability of the asphaltenes in their respective crude oils that may help to predict the mechanisms by which an oil alters wetting.³

Solubility of Asphaltenes

How stable are the asphaltenes in their crude oil environment? How good a solvent is an oil for its asphaltenes? Traditionally these questions have been answered by assigning solubility parameters to oil and asphaltenes and noting the difference between them.^{4,5} Solubility parameters which are used in thermodynamic models have the disadvantage that they can be measured only for pure compounds. For simple mixtures, they can be calculated, but not for complex mixtures, such as crude oils and their asphaltenes, for which estimates are used. For non-polar molecules, there is a linear relationship between solubility parameter and a simple function of refractive index.

Both quantities, solubility parameter and RI, are related to van der Waals forces between non-polar molecules. For polar molecules, solubility parameters can include the effects of dipolar and hydrogen bonding interactions. We make the important simplifying assumption that it is mainly the non-polar van der Waals forces that are responsible for separation of asphaltenes from the oil phase and that other interactions can be neglected. In that case, RI is equivalent to solubility parameter as a measure of solvent properties.¹

RI of Mixtures

If there are no significant changes in volume on mixing, the mixing rules for the refractive index are very simple, as shown by **Eq. 1**.

$$\frac{n^2 - 1}{n^2 + 2} = \sum_i f_{\text{volume},i} \left(\frac{n_i^2 - 1}{n_i^2 + 2} \right) \quad (1)$$

where n = mixture refractive index, n_i = refractive index of i in the mixture.

RI of Crude Oils

In **Fig. 1**, measured values of RI are plotted for mixtures of a sample of Spraberry crude oil and n -heptane. This sample of Spraberry was of medium gravity (31.1° API) and had only 0.8% n -pentane asphaltenes. Examples of each mixture were examined microscopically and no asphaltenes were found in any of them. Note that the oil sample was too opaque to allow direct measurement of RI, but that $RI_{\text{oil}} = 1.485$ can be found by extrapolation to a

Figure 1. Linear trend of RI with volume fraction of crude oil mixed with n -heptane.

volume fraction of 1. The measured data can be read on either scale. The straight line is a least-squares fit to the measured data with $r^2 = 0.999$. The presence or absence of precipitate is verified by microscopic observation of a drop of each mixture at a magnification of 45X.

Although we can treat the crude oil as a single component, as in Fig. 1, it is also useful to consider the contributions of certain fractions to the mixture RI. In general, paraffinic compounds are the lowest RI material, cyclic compounds are higher in RI than linear ones of similar molecular weight, and aromatics are higher still (**Fig. 2a**). The resin and aromatic fractions contain some of the highest RI material as shown in **Fig. 2b** for resins and asphaltenes separated from an oil sample from Prudhoe Bay.

Figure 2. RI of various components of crude oils: (a) hydrocarbon molecules and (b) resin and asphaltene fractions from A-93 crude oil.

Asphaltenes can be separated from the remaining oil components (maltenes) by addition of sufficient *n*-heptane. After removal of the precipitated asphaltenes by filtration, the maltenes can, in principle, be recovered by evaporating off the excess precipitant. In **Fig. 3**, RI is plotted—to reflect that distinction—as a function of the following volume fractions: $f_v = 0$ for pure *n*-heptane, $f_v = 0.93$ for A-95 maltenes, and $f_v = 1$ for maltenes plus asphaltenes (A-95 crude oil). The line between *n*-heptane and A-95 maltenes (f_v from 0 to 0.93) shows the RI of mixtures between them. There is another line between maltenes and oil (f_v from 0.93 to 1) that represents the contribution of asphaltenes to RI_{oil} . A

Figure 3. RI of A-95 crude oil, A-95 maltenes, and mixtures with *n*-heptane.

dashed line connects A-95 oil with *n*-heptane. Since asphaltenes are the highest RI material present in the oil, the maltenes lie below the dashed line.

RI at the onset of asphaltene flocculation/precipitation

We have shown previously that asphaltenes appear at a mixture refractive index that is characteristic of a particular oil and precipitant.^{1,2} By addition of varying amounts of solvents (toluene or α -methylnaphthalene), the volume fraction of oil and the concentration of asphaltenes can be varied over a wide range of values, but the RI at which precipitation is first observed, the P_{RI} , remains unchanged. This value is shown as a horizontal band in plots of RI vs. $f_{v,oil}$, as in **Fig 4**. It is characteristic of colloidal dispersions that their stability is governed by some aspect of their environment, in this case RI, unlike solubility of a chemical compound that is limited by its own concentration in the solution.

Figure 4. P_{RI} is RI at which precipitation is first observed, as shown for *n*-heptane mixtures with (a) A-95 crude oil from Prudhoe Bay and (b) an asphaltic oil from California.

RI of mixtures during heptane titration

A generalized version of the RI vs. volume fraction plots for mixtures of crude oil and *n*-heptane is shown in **Fig. 5**, following the path of a typical heptane titration experiment. Initially heptane is added to the whole crude oil. Before the onset of precipitation, mixture RI values lie on the line between RI_{oil} and $RI_{heptane}$ (Fig. 5a). In this region, mixtures are stable with respect to dispersion of the asphaltenes. Precipitation is first observed when the mixture RI reaches P_{RI} (Fig. 5b). As additional heptane is added, asphaltenes separate from the mixture. RI values in the unstable region now should lie below the oil-heptane line and, as additional precipitation occurs, should approach the line connecting maltenes and heptane (Fig. 5c). An important element of this picture that has not been considered in previous studies of asphaltene precipitation is the contribution of the asphaltenes themselves to the RI and thus the solvent quality of the stable oil.

(a) Beginning of the heptane titration experiment.

(b) Precipitation begins when $RI = P_{RI}$.

(c) RI of maltene + heptane mixtures in precipitating region.

Figure 5. Path of RI vs. volume fractions in crude oil mixtures with heptane.

Addition of solvents

In previously reported experiments, toluene and other solvents were added to A-93 crude oil samples prior to heptane titration.² The mixtures in which the onset of asphaltene instability was identified had a wide range of percentage asphaltene and the volume fractions of oil varied as well, but the value of P_{RI} was relatively constant for a given oil and precipitating agent. This situation is illustrated in **Fig. 6**. Initially oil is mixed with solvent and mixture RI values fall on the line joining RI_{oil} and $RI_{solvent}$ where the solvent can be any high-RI hydrocarbon. At some point, illustrated here for a 50:50 (by volume) mixture of oil and solvent, precipitant is added. RI values now decrease along the straight line joining the arbitrary mixture and pure precipitant, as shown.

Instability is observed when the RI drops below the onset value of P_{RI} ; some deviation in RI can be expected as asphaltenes separate from the liquid mixture. Although the solvent shown here has a higher RI than the oil does, it could be equal to or lower than the RI of the oil. Similarly, for different oils with a particular solvent, $RI_{solvent}$ can be either higher or lower than RI_{oil} . The slopes of the lines and volume fractions at P_{RI} will vary accordingly.

Figure 6. Path of RI vs. volume fractions in crude oil mixtures with a solvent of higher RI and heptane.

Reversibility of asphaltene precipitation

Whether or not asphaltene precipitation is reversible in a true thermodynamic sense is the subject of substantial debate (see, for example, ref. 6, and references cited therein). Some of the disparities found in the literature are undoubtedly due to slow kinetics of dispersion and flocculation. Additional differences may be related to the presence of a certain amount of inorganic material in crude oils that is separated with and misidentified as asphaltene.

Figure 7. Because of the separation between asphaltenes and maltenes that occurs below P_{RI} , the process indicated by arrow 1, where heptane is added to oil, is not the inverse of arrow 2, where oil is added to heptane, even though the final volume fractions are identical.

Figure 8. Addition of toluene to a mixture of A-95 crude oil and n-heptane ($f_{v,oil} = 0.25$) demonstrates that the asphaltenes disappear at the same RI at which they originally appeared.

A third important source of confusion may arise because of the contribution of asphaltenes themselves to the mixture RI and failure to account for the difference in solvent quality between maltenes and oil. This is most readily explained with an illustration (**Fig. 7**). It is reasonable to expect that a solution prepared by addition of heptane to oil (arrow 1) should be identical to another prepared by adding oil to heptane (arrow 2), but the diagram shows that even though the volume fractions in the two mixtures are identical, asphaltenes are stable in the first solution and unstable in the second. Again, it is the effect of the asphaltenes themselves on the solvent properties of the oil that account for this apparent lack of reversible behavior.

A different test of reversibility is shown in **Fig. 8**. Mixtures of A-95 and heptane were prepared and examined for RI and presence or absence of asphaltenes (dotted line with open and closed circles). One of these mixtures ($f_{v,oil} = 0.25$), well into the unstable asphaltene region with asphaltene precipitate separated from maltenes was selected. Toluene was added in increasing amounts to this mixture until the separate asphaltene phase disappeared. Both appearance and disappearance occur over the same narrow range of mixture RI values. In this test, asphaltene precipitation appears to be completely reversible.

2. Wetting Evaluation

The potential importance of asphaltene characterization to understanding the influence of crude oils on wetting can be investigated using the RI tools described in this summary. The influence of asphaltenes can now be evaluated as a function of their state of dispersion. These tests are in progress.

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