Contact Angle Hysteresis at Smooth and Rough Surfaces

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Background

Reservoir wettability is widely recognized as having a dominant influence on displacement for many reservoir processes, the most widely applied being waterflooding. The factors that determine wetting behavior depend on numerous interacting phenomena, many of which, despite their technological and economic significance, are far from understood. Contact angles measured for crude oil against brine on smooth mineral surfaces have been used to characterize wettability, but links between contact angle and oil recovery are fraught with uncertainties. Factors that need to be considered include departure from smooth, chemically homogeneous surfaces, the effect of adsorption from crude oil on surface properties, contact angles, pore geometry, and the interactions that determine capillary pressures, flow behavior, and initial and residual saturations. Relative permeability is a key parameter in reservoir simulation. A common approach to allowing for the complexities of specific reservoirs is to obtain data on carefully handled and prepared core plugs with live reservoir fluids at reservoir temperature, pore pressure, and confining pressure. The steps in this procedure involve numerous decisions on protocol that range from coring procedures and preservation to laboratory testing. However, no systematic study or tests of the reproducibility of reservoir conditions data has been reported. Examination of reservoir rocks by petrographic and SEM imaging demonstrate the complexity of pore space with respect to the chemical heterogeneity of pore surfaces and roughness. The number of publications on the effects of surface roughness and chemical heterogeneity on wetting has grown exponentially in relation to a variety of practical problems. However, comparatively little attention has been paid by the petroleum industry, over the last few decades, to the basic controls on wetting even though it is a governing factor in oil recovery. Overall, studies of the effects of surface roughness and chemical heterogeneity are becoming increasingly disconnected and are surprisingly contentious with respect to interpretation of the classic work of Wenzel (1936), Cassie and Baxter (1944), and Cassie (1948). (e.g. see Gao and McCarthy, 2007; McHale, 2007; Marmur and Bittoun, 2009; Milne and Amirfazli, 2012). A review of some developments with respect to the effects of surface roughness on contact angle and capillary displacement pressures will be presented.

Contact angle hysteresis and surface roughness

Erbil et al. (1999) identifies three main techniques for measurement of contact angles on nominally flat solid substrates. The most common is the sessile drop or captive bubble. The other two are force measurements by the Wilhelmy plate and the inclined plate. Advantages and disadvantages of each method were discussed. Erbil et al. (1999) point out that the apparent simplicity of contact angle measurement is misleading and there is still controversy over the reliability and reproducibility of the data. Cassie (1948) concluded that “It is doubtless the difficulty of producing a smooth surface gives rise to so many different published values for the contact angles of a given liquid and solid.”

Measurements of contact angles on drops

If contact angles are single valued, as implied by Young’s equation, the contact angle is single valued and will be referred to as the *intrinsic* angle. Advancing and receding contact angle measurements made at flat surfaces by direct measurement of the angle at which the profile of the fluid/liquid drop intersects the solid, will be referred to as *apparent* contact angles. Contact angles will be discussed in terms of air and a liquid with contact angle measured through the liquid phase unless stated otherwise. Much of the reported *apparent* contact angle data was obtained using a goniometer to measure projected contact angles at either side of a drop. It is now common to determine the *apparent* contact angles at opposite sides of the drop by algorithms which match the drop profiles.

Measurement of definitive *apparent* advancing and receding contact angles for drops requires a controlled method of growing or diminishing the drop volume. In most studies, the interface curvature of the drop is positive but very low. Measurement of consistent receding contact angles for drops is often reported to be significantly more difficult than for advancing contact angles **(**Cassie, 1948, Erbil, 1999**)**. Cassie (1948) stated: "The instability of receding contact angles is the real bar to progress in the theory of water repellency." A fundamental problem with drops on rough surfaces is that the capillary pressure at the drop surface varies with height according to gravity, but is at a slightly excess pressure that is greatest around the perimeter defined by the three phase line of contact. If the solid is wetted by the liquid so that some bulk liquid is retained by surface grooves and asperities behind the receding interface and the *apparent* receding angles will be very low. A drop with low *intrinsic* angle will disappear if set on grooves of infinite length. For drops that exhibit finite *apparent* contact angles, changes of angle with drop size have often been reported, but the effects are not consistent. Marmur and Bittoun (2009) concluded that most contact angle measurements on rough surfaces are invalid because of insufficient difference between the scale of the microscopic roughness and the drop size.

Capillary rise in cylindrical tubes.

An alternative technique for determining contact angle hysteresis is to determine advancing and receding contact angles at rough surfaces from capillary rise (Morrow 1975). The capillary rise method gives *effective* contact angles that correspond to average values of *apparent* angles for the complete perimeter of the meniscus. Cylindrical tubes, the most obvious choice of tube cross-section, are commercially available in wide ranges of diameters for many of the manufactured polymeric solids. The scale of microscopic roughness to meniscus dimensions and curvature, and the effect of interface curvature on *effective* contact angles can be adjusted through choice of tube size. The problem of obtaining consistent *effective* receding contact angles for low *intrinsic* angles is essentially solved because the negative curvature of the meniscus can balance the negative curvature of any bulk liquid retained in the vicinity of the drop perimeter. Numerous values of *effective* advancing and receding values of contact angle for a single tube can be obtained rapidly from capillary rise by incremental change in meniscus location along the tube simply by raising or lowering the tube with respect to a free liquid surface. These measurements provide a check on the statistical uniformity of the tube surface. Such large data sets provide well-tested limits of confidence.

The effect of roughness on contact angle can be investigated by roughening the internal surface of the tubes. An SEM image of a roughened internal surface of a tube is shown in Fig. 1a. For details of the roughening procedure and subsequent cleaning see Morrow (1975). Between the limits defined by contact angle hysteresis, the tube can be raised or lowered so that the interface curvature and *effective* contact angle change continuously, but the height of rise above the free liquid surface is fixed. Advancing and receding *effective* contact angles from measurements of capillary rise of liquids in PTFE tubes with roughened internal surfaces are plotted against intrinsic angles in Fig. 2; the error bars are typical of all of the data. No problem was encountered in obtaining definitive vales of the effective receding contact angles. The results were extended to intrinsic contact angles of up to 180° by plotting data in terms of the supplementary angles that apply to the gas phase (see gray-tone triangles in Fig. 2). The reciprocity of the angles through the liquid phase and the supplementary values through the gas phase for *intrinsic* angles ranging from 72° (alpha-bromo-naphthalene) and 108° (water) supports this interpretation. Measurements for 11 tube sizes showed no effect of curvature on the *effective* contact angles.

The lower and upper limits of *effective* contact angles (θ_R and θ_A, respectively) for any given *intrinsic* contact angle are shown in Fig. 3 as solid lines, obtained by extrapolating a straight line through the receding and advancing values. Any error in assuming that very low contact angles are zero is small, especially if cosines are considered (e.g. cos 20° = 0.94). The hysteresis is largest for *intrinsic* contact angles in the range of about 60° to 120°.

Capillary rise in tubes of uniform geometry and chemistry in cross-section - the MS-P method

Application of the capillary rise method to determine interface curvature is by no means restricted to cylindrical tubes. Measurement of capillary rise in tubes assembled from combinations of flat surfaces and rods in combination with analytic solutions by the MS-P method allow determination of *effective* contact angles for a completely new class of capillary surfaces (Mason et al, 1983). Selected tube shapes can include the possibility of dual occupancy of the pores because of capillary rise or depression in corners. The tubes can have open or closed perimeters. The MS-P analysis is founded on virtual work arguments that provide a direct relationship between changes in surface free energy and force balance along the three phase line of contact. The method provides a powerful approach to analysis of the many linear models of surface roughness that have been posited in the literature on wetting. The term linear is used in the sense that the cross section of the tube and the chemical properties are uniform with respect to tube cross section. The ratio of scale of roughness and chemical heterogeneity to the meniscus that spans the tube (referred to as the main terminal meniscus in situations where they are connected to arc menisci in corners) can be tested at will. Thus, the method allows investigation of the effect of different forms and scales of roughness on wetting (Raeesi, 2012).

The MS-P method also has application to surfaces with statistically consistent but random areal microscopic roughness (a relaxation of the condition that a tube must have precisely constant cross section in geometric and wetting properties) provided the direction of movement and the associated advancing and receding angles are taken into account. As with many problems involving interfaces and hysteresis, path-dependency is all important. For roughened plates, the alternative approach of measuring force by the Wilhelmy plate method would also readily provide definitive *effective* contact angles for advancing and receding three-phase lines of contact.

Comparisons of contact angle measurements at rough surfaces

The subject of effect of roughness on wetting was recently reviewed by Quéré (2008) but data obtained from capillary rise, application of the MS-P method, and numerous discussions of the effect of wetting on the capillary properties of porous media were not considered. It was pointed out that scatter and reproducibility of receding contact angles in particular was an unsolved problem. For rise in tubes, the effect of evaporation from drops, discussed in detail by Erbil et al. (1999), is not an issue because tubes provide a locally controlled-humidity environment.

Comprehensive comparison between *apparent* and *effective* contact angles at rough surfaces has not been previously reported. From the collected historic data plotted in Fig. 3, it is seen that a large body of reported *apparent* contact angles for liquid drops at surfaces of various substrates and with variously described roughness all falls within the hysteresis limits of the *effective* contact angles obtained by the capillary rise method for internally roughened PTFE tubes. For some of the data, such as that of Cassie and Baxter (1944), Bartell and Sheppard (1953a and b), and Sheppard and Bartell (1953), there is modest hysteresis (usually less than 10º) in the reported contact angles at smooth wax surfaces; the advancing and receding angles at roughened surfaces are then plotted against the respective values for smooth surfaces.

Bartell and Shepard (1953a and b) and Sheppard and Bartell (1953) reported *apparent* advancing and receding apparent contact angles for drops on rough surfaces of defined geometry. The surfaces were prepared by scribing orthogonal grooves on wax to give pyramidal structures (see Fig. 2b) with slopes determined by their height and width. Hysteresis was independent of the height of the pyramids, but showed sensitivity to the slope of the pyramids because the slope sets the range over which contact angles can hinge between advancing and receding conditions. The range of hysteresis was determined for slopes of 30°, 45° and 60°. For the pyramidal surfaces, the data for the 60° slope (see Figure 3) gave the largest hysteresis and closest match to, but still fell within the bounds of, the data for roughened PTFE tubes.

The closest comparison to the *effective* contact angle data for roughened tubes for a range of *intrinsic* angles is given by *apparent* contact angles reported for solid surfaces prepared from blends of AlkylKetene Dimer (AKD)/ and DiAlkylKetone (DAK) (Shibuichi et al., 1996). Smooth surfaces of the AKD/DAK blends were prepared by cutting into the interior of a block of the solidified blend. Shibuichi et al. (1996) described the surfaces prepared in this way as having fractal roughness (see Fig 2c). The wetting behavior of mixtures of water and 1,4-dioxane gave intrinsic contact angles measured at the smooth surfaces that ranged from 40° for 20% water, to 109° for pure water. *Apparent* contact angles were determined by allowing liquid drops to fall from a small height onto the rough surfaces of the AKD/DAK blends, followed by finger tapping of the substrate before measuring an angle. Relationships between apparent contact angles measured at the rough so-called fractal surfaces and *intrinsic* angles measured on smooth surfaces were reported for three AKD/DAK blends. The measured *apparent* contact angles were described as equilibrium values. The angles for AKD/DAK blends fall within the bounds set by the *effective* advancing and receding angles determined from capillary rise in roughened PTFE tubes (see Fig. 3). The largest spread in the *apparent* contact angle data for the AKD/DAK rough surfaces is in the intermediate range of *intrinsic* contact angles from about 70° to 110°. The comparison shown in Fig. 3 indicates that the *apparent* contact angles for drops reported by Shibuichi et al. (1996) are all intermediate to the *effective* advancing and receding contact angles obtained by capillary rise in roughened tubes obtained for a different solid

(PTFE) and an entirely different method of generating roughened surfaces. *Apparent* contact angles measured by Tamai and Aratani (1975) for roughened silica glass plates (Fig. 1d) also fall within this range.

The literature contact angle data shown in Fig. 3 were obtained for a range of types of random and regular roughness. From the data considered to date, it is concluded that determination of *effective* advancing and receding contact angles from rise in tubes provides a distinctly more consistent account of the limits of contact angle hysteresis than given by *apparent* angles for drops no matter what selectivity is applied.

Effect of contact angle hysteresis on capillary pressure in porous media

It is well-known that relationships between capillary pressure and saturation for a porous material exhibit path-dependent hysteresis. The hysteresis is basically caused by instabilities in fluid configurations that result in pressure versus saturation paths being irreversible (Haines, 1930). A comprehensive set of hysteresis data for refined oil/brine/Bentheim sandstone is shown in Fig. 4 (Raeesi, 2012). The data are for an intrinsic contact angle of zero (i.e. spreading) or, at least, to *effective* receding and advancing contact angles of zero.

The next consideration is the effect of wettability on capillary pressure hysteresis when the contact angle is finite. Capillary pressure data for porous PTFE with intrinsic angles for liquid against air ranging from zero to 108° degrees are summarized in Figs. 5a and b. An electron micrograph clearly shows that the pore surfaces are rough (see Fig. 1f). The drainage curves shown in Fig. 5a are approximately proportional to the receding contact angles measured at rough surfaces, with capillary pressures being essentially unchanged for contact angles up to about 60 degrees. This result is consistent with receding angles being zero, or nearly so, for *intrinsic* contact angles ranging up to about 60 degrees. One implication of this result is that the practice of reducing injection pressures by a factor of cos 40° (= 0.766) in estimating pore throat sizes from mercury injection data is not justified for porous materials with rough surfaces. A comparison of *apparent* receding contact angles from roughened tubes with *apparent* contact angles Φ_R for the porous media, given by setting cos Φ_R to the reduction in drainage curvature is shown in Fig. 5c.

Advancing angles at rough surfaces are zero, or nearly so, for contact angles lower than about 30° and then increase markedly with respect to the intrinsic angles (see Fig. 2). This is consistent with reported independence of capillary imbibition pressures for low contact angles, but marked sensitivity of spontaneous imbibition for intrinsic angles ranging from about 30° to 62° (see Fig. 5b). Measured imbibition pressures were approximately proportional to the advancing angles measured at rough surfaces. Imbibition pressures are highly sensitive to contact angle and are estimated to change sign when *intrinsic* contact angles becomes greater than about 62° (see Fig. 5b). The *apparent* advancing angles, Φ_A, for the imbibition data for the porous media are in remarkably close agreement with the advancing angles measured at rough surfaces (see Fig. 5d). The added complication of the effects of converging/diverging pore shapes, which many pore models show to be highly significant in theory, appears to be of secondary importance compared to the effect of surface roughness on contact angle.

Effect of CA hysteresis on drainage and imbibition for crude oil and brine

The distribution and displacement of fluids in hydrocarbon reservoirs involves the effects on wetting related to surface roughness, chemical heterogeneity, and pore geometry, plus additional and far more complex wetting phenomena. Reservoir wettability is a broadly-used term that depends on crude oil/brine/rock interactions. These include the effects of rock mineralogy and pore structure, the distribution of connate brine, the crude oil, and the history of contact with injected water. Oil recovery depends on movement of interfaces and capillary trapping under highly complex conditions. The effect of adsorption from crude oil can have a dominant effect on oil recovery by water flooding and is crucial to recovery from fractured reservoirs by spontaneous imbibition.

In a widely accepted model of reservoir wettability, described by Salathiel (1973) as mixed wettability, it is postulated that the pattern of adsorption from crude oil is determined by the fraction of the rock surface that is overlain by crude oil. Areas overlain by bulk water are protected from adsorption and remain strongly water wet. Thus a pattern of chemical heterogeneity is set up that is strongly dependent on the saturation and detailed distribution of connate water. The patterns will be directly determined by regions of pore space such as micro-porosity, crevices, and other features related to pore structure and roughness which retain bulk water at high capillary pressures.

The mixed wettability condition has been modeled as consisting of a distribution of very strongly water wet and very strongly oil wet surfaces (Salathiel, 1973; Kovsec et al., 1993). However, both contact angle measurements and spontaneous imbibition measurements show that adsorption from crude oils can exhibit a wide range of wetting states. Contact angle measurements at specific smooth mineral surfaces provide indication of the wetting changes that can be induced by adsorption for specific crude oil/brine combinations. The angles have been shown to depend on the crude oil, the pH, the brine composition, the mineral and the condition of the mineral surface and complex effects of temperature and time of contact. Advancing contact angles after adsorption from crude oil can range from low, but finite angles, up to a maximum of about 150° even for oils that contain destabilized asphaltenes (Yang et al., 2003).

The drainage and imbibition data shown in Fig. 4 for refined oil correspond to very strong water wetting. For crude oils taken from 29 sandstone reservoirs, 25% of advancing contact angles on quartz at reservoir temperature were below 20° (Treiber et al., 1972). Low effective contact angles for crude oil can also be inferred from capillary pressure data.

Exploratory drainage and imbibition data for three Bentheim core plugs using refined oil (Plug 2), crude oil with nominally no aging time (Plug 3), and crude oil after 7 days aging at room temperature (Plug 4) are presented in Figs. 6a and b, respectively. The data were scaled for differences in interfacial tension. Apart from the drainage of refined oil being slightly low at high brine saturation, the three drainage curves shown in Fig. 6a are in agreement, showing that there is no significant effect of wetting on drainage. The corresponding imbibition data are shown in Fig. 6b. There is no difference between the imbibition curves for Plugs 2 and 3. For Plug 4 (aged with crude oil for 7 days), the imbibition capillary pressure curve is lower than for the other two plugs (the pressure for Plug 4 was not lowered sufficiently to establish residual oil saturation). From consideration of the effect of roughness on effective contact angles shown in Fig. 2 and the form of the capillary pressure data shown in Fig. 5 the following inferences can be drawn. For drainage, the *effective* receding angles are very low for all 3 cores. For imbibition, the *effective* advancing contact angle for the crude oil without aging (Plug 3) is less than about 30°. For Plug 4 (aged with crude oil for 7 days), the *effective* advancing angle, from inspection of the shifts in curvature for the imbibition curves with contact angle shown in Fig. 5b, is about 40°.

From consideration of contact angle data in Fig. 2 and capillary pressure data in Fig. 6b, it is concluded that the effect of roughness and the inter-related distribution of bulk water can cause effective contact angles for crude oil to be low. Aging with crude oil at elevated temperature will likely cause further depression of the imbibition curvatures and may also affect the drainage curvatures. It should also be noted that aging a core at decreasing levels of initial water saturation causes marked decrease in rate and extent of spontaneous imbibition (Xie and Morrow, 2001). Thus connate water distribution is a key parameter of reservoir wettability that presents distinct limitations on assessment of reservoir wettability simply from some form of contact angle measurement alone.

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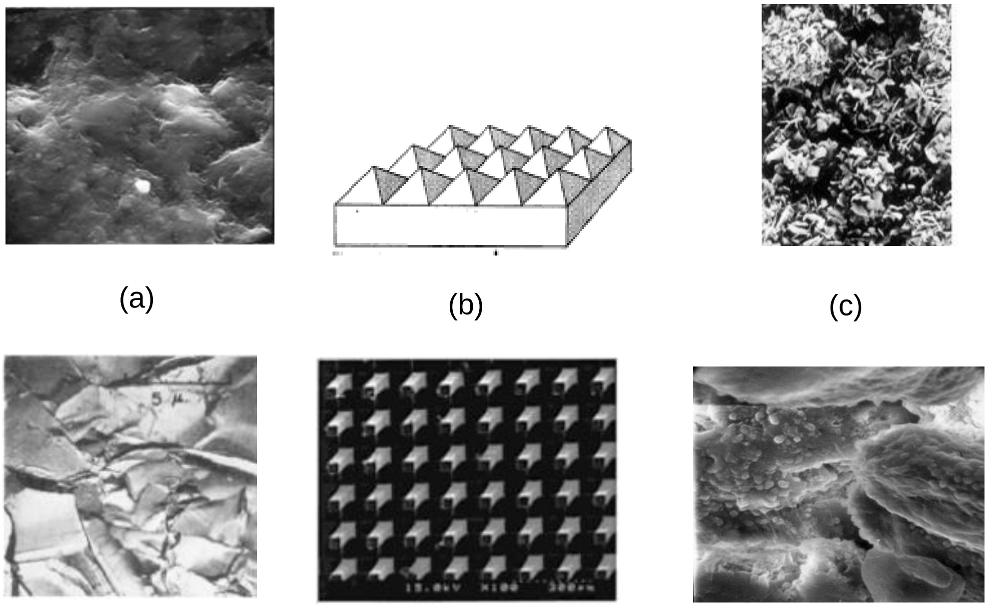

(a) (b) (c)

(d) (e) (f)

Figure 1. Examples of rough surfaces: (a) internal surface of a roughened PTFE tube (Morrow, 1975), (b) Pyramids scribed on wax (Bartell and Shepard, 1953a), (c) fractal roughness (Shibuichi et al., 1996), (d) abraded silica (Tamai and Aratani, 1972), (e) pillared surface (Yoshimitsu et al., 2002) (f) pore scale roughness of PTFE.

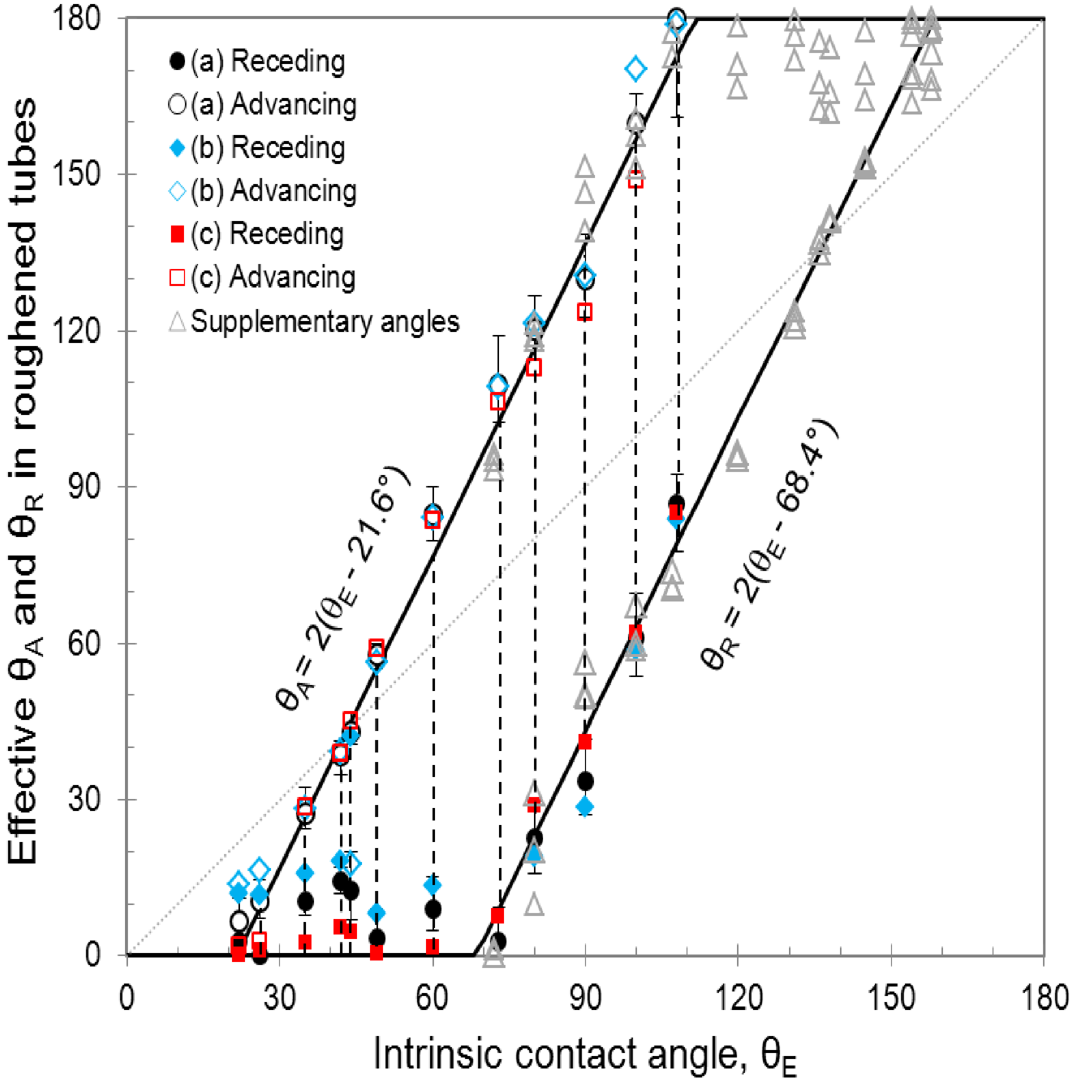

Figure 2. Effective receding and advancing versus intrinsic contact angles determined from capillary rise in tubes: (a) sufficiently roughened with fine particles (b) severely roughened with medium-size particles (c) severely roughened with coarse particles. Receding contact angle data is approximated as zero for up to 68° intrinsic angle, the fluctuation in the low (or high) contact angles of up to 20° correspond to only small change in their cosines > 0.94.

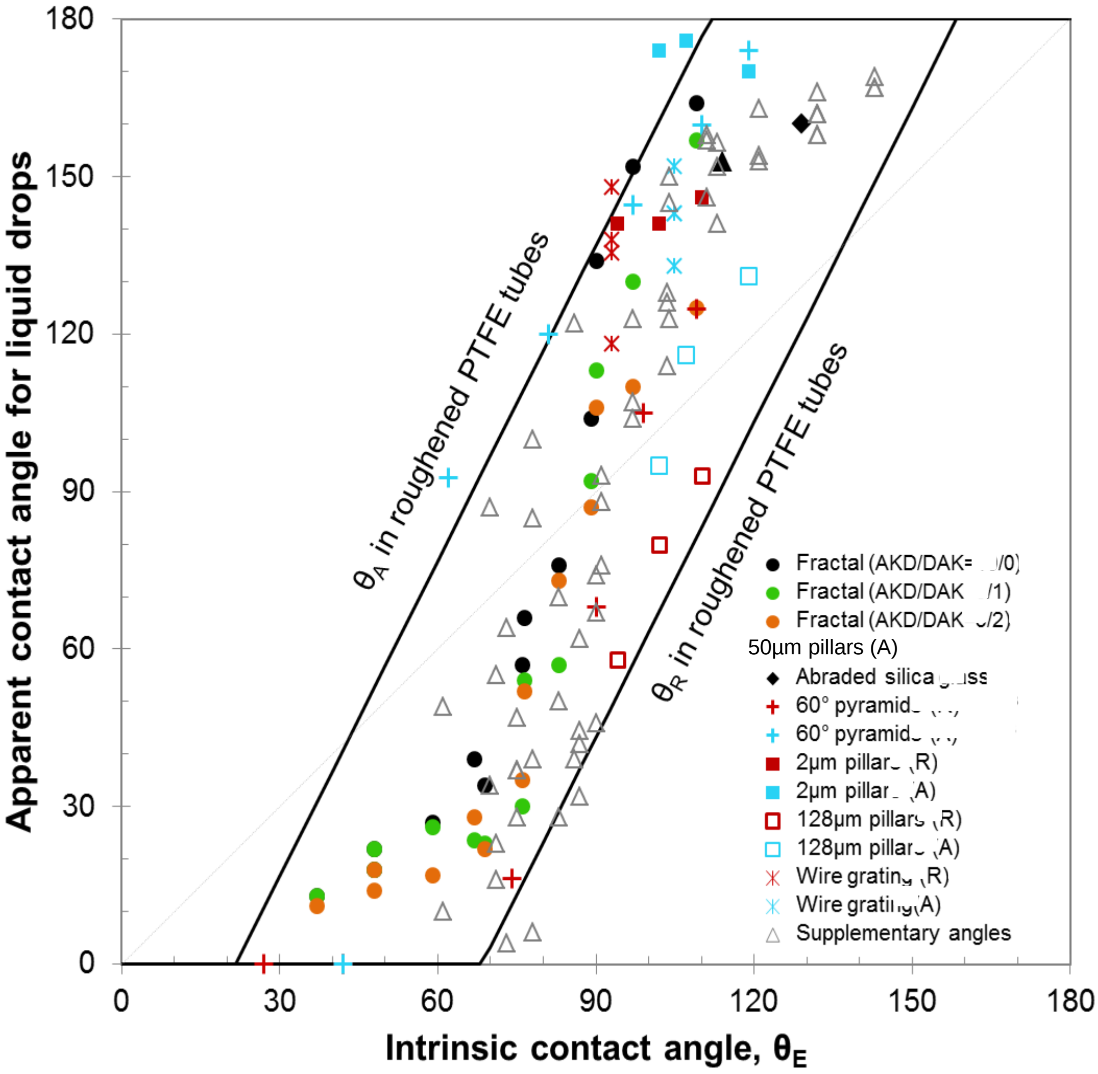

Figure 3. Comparison of apparent contact angles reported for liquid drops at different rough surfaces, or for a hydrophobic wire grating, with the range of hysteresis determined from capillary rise in roughened PTFE tubes. (R) and (A) stand for receding and advancing contact angles, respectively.
(●●● Shibuichi et al., 1996; ▲ Yoshimitsu et al., 2002; ◆ Tamai and Aratani, 1972; ++ Bartell and Shepard, 1953a,b and Shepard and Bartell, 1953; ■■□ □ Öner and McCarthy, 2000; XX Cassie and Baxter, 1944)

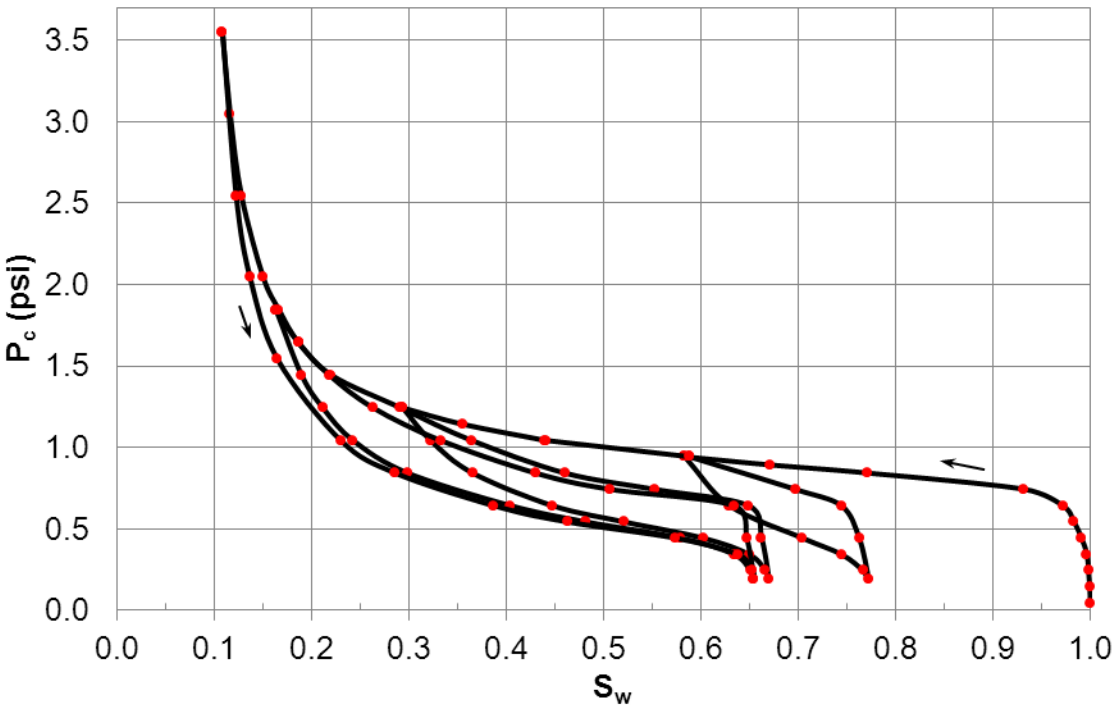

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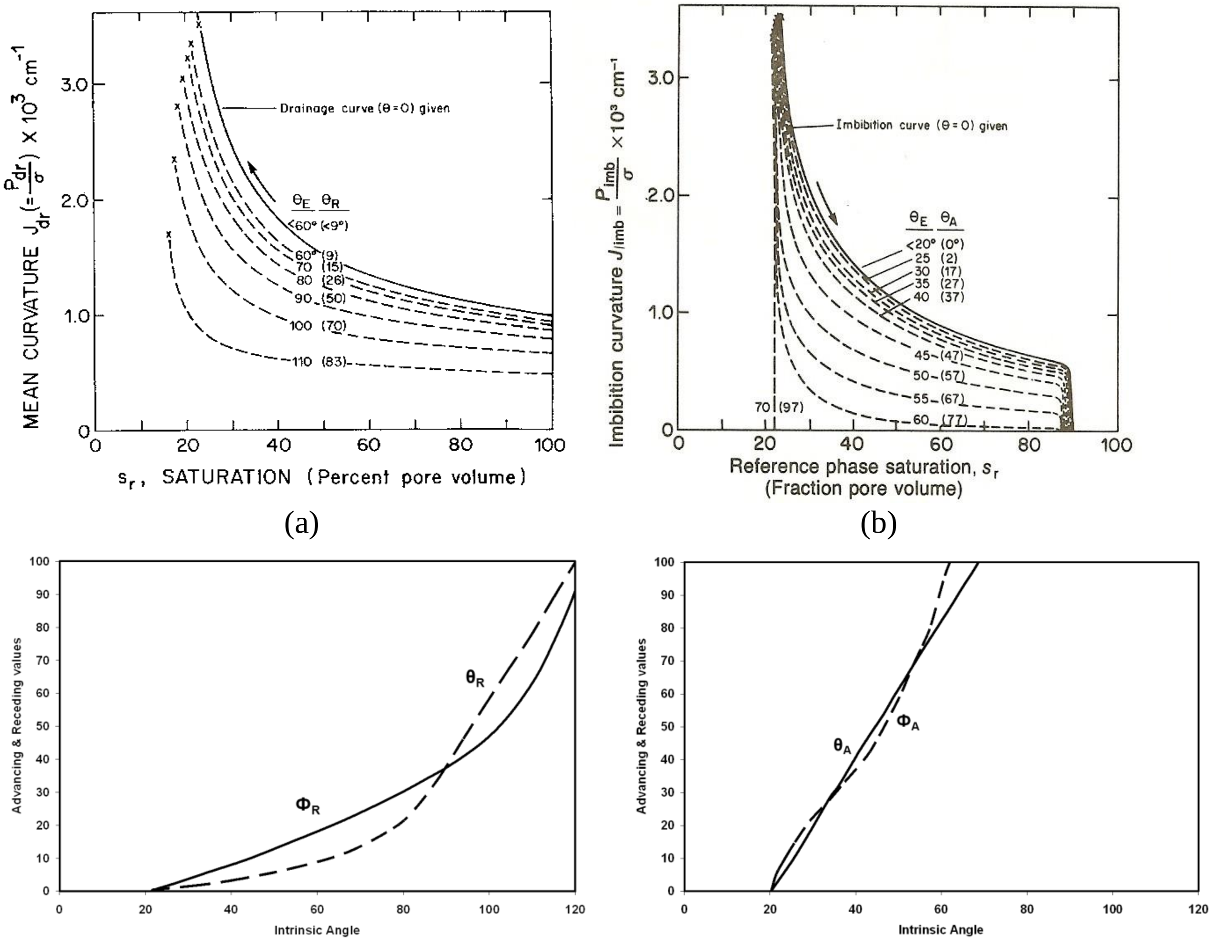
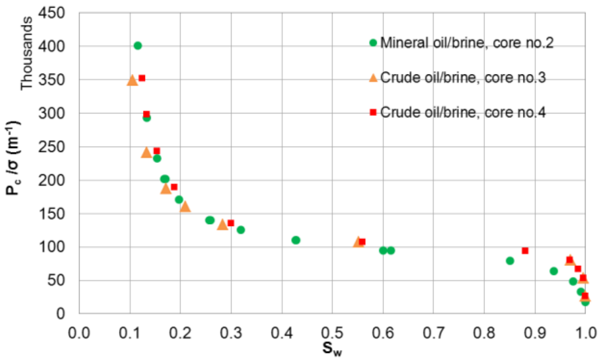
Figure 4. Capillary pressure hysteresis data including scanning loops for very strongly wetted (water/air) Bentheim sandstone. Fluid configurations for P_c - S_w co-ordinates are strongly path dependent.

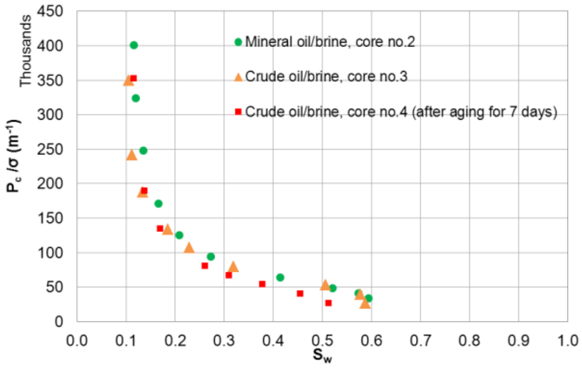


(a) (b)

(c) (d)

Figure 5. Change in (a) drainage and (b) imbibition curvatures (capillary pressure divided by surface tension) based on correlation of data for 6 PTFE cores for *intrinsic* contact angles ranging from Θ_E <20° to 110°. Angles shown in parentheses are the receding angles at rough surfaces in (a) and the advancing angles at rough surfaces in (b); (c) Comparison of Φ_R from drainage capillary pressure data and receding angles at rough surfaces versus *intrinsic* contact angle; (d) Comparison of Φ_A from imbibition capillary pressure data and *effective* advancing angles at rough surfaces versus intrinsic contact angle; (cos Φ_R and cos Φ_A are based on proportionality to the reduction in curvature for drainage and imbibition respectively (the cylindrical tube model with distinction between drainage and imbibition) with increase in *intrinsic* contact angle) (after Morrow, 1976)





(a) (b)

Figure 6. Capillary pressure drainage and imbibition curves for a Bentheim sandstone core: (a) primary drainage data for mineral oil/brine and crude oil/brine (b) imbibition data for the same liquid pairs. Capillary pressure is scaled to IFT ($\sigma_{\text{mineral oil-brine}}$=45.1 mN/m, $\sigma_{\text{crude oil-brine}}$=25.4 mN/m).