

## Predicting two- and three-fluid capillary pressure-saturation relationships of porous media with fractional wettability

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**Abstract.** Knowledge of the capillary pressure-saturation ( $P_c$ - $S$ ) relations of porous media is essential for the research and management of multiphase flow and transport. Indirect methods have often been used to predict  $P_c$ - $S$  curves, since the actual measurement of all  $P_c$ - $S$  curves may be cumbersome. Existing methods to predict the  $P_c$ - $S$  relations for porous media with fractional wettability, however, are generally inadequate. This paper reports on methods to quantify  $P_c$ - $S$  curves of such media that contain two or three fluids (air, oil, and water). The prediction of oil-water  $P_c$ - $S$  relations from air-oil or air-water  $P_c$ - $S$  data through mere scaling is not possible since the oil-water capillary pressure may be positive or negative in fractional wettability media. We successfully predicted the oil-water  $P_c$ - $S$  curve using a linear transformation of air-oil  $P_c$ - $S$  data. In three-fluid media with fractional wettability the prediction of three-fluid from two-fluid  $P_c$ - $S$  relations using only Leverett's assumption is unreliable, since both water and oil act as intermediate fluid. We predicted the three-fluid oil-water  $P_c$  from two-fluid oil-water or linearly transformed air-oil  $P_c$ - $S$  data. The three-fluid air-oil  $P_c$  could be readily predicted from the two-fluid air-oil  $P_c$ - $S$  relation for a variable oil saturation and a constant water saturation. In contrast, when the water saturation was varied, at a constant oil saturation, the air-oil  $P_c$  could only be predicted using an empirical correction for the two-fluid air-oil  $P_c$ - $S$  data. The three-fluid air-water  $P_c$  is obtained as the sum of the oil-water  $P_c$  and the air-oil  $P_c$  (both water and oil pressures are measured with respect to atmospheric pressure).

### Introduction

The simulation of multiphase fluid flow in the subsurface requires that the capillary pressure-saturation ( $P_c$ - $S$ ) relations of the porous medium be known for all fluid pairs. The measurement of the relevant  $P_c$ - $S$  curves for two-fluid and, especially, three-fluid media can be very cumbersome. Indirect methods, based on scaling and Leverett's assumption, have often been used to predict  $P_c$ - $S$  curves from data that are already available or can be measured more easily [Lenhard and Parker, 1988; Ferrand et al., 1990; Bradford and Leij, 1995a]. Existing theories for the prediction and modeling of oil-water  $P_c$ - $S$  relationships are generally based on the limiting assumption that the medium (solid) is strongly wetted by one fluid (e.g., water) [Corey, 1986]. Additionally, in air-oil-water systems it is assumed that the intermediate wetting fluid (e.g., oil) forms a continuous layer between the wetting (water) and nonwetting (air) fluids [Leverett, 1941; Lenhard and Parker, 1988]. These assumptions do not hold for many natural systems, as will be discussed below.

The wettability of natural porous media varies often with position due to the presence of (immobile) adsorbed liquid layers [Adamson, 1990] and nonuniform adsorptive properties [Fatt and Klikoff, 1959]. Anderson [1987] reported that coal,

graphite, sulfur, talc, talclike silicates, and many sulfides have probably a neutral wettability or are oil-wet. On the other hand, common aquifer materials, such as quartz, carbonates, and sulfates, are strongly water-wet. The wettability of originally water-wet porous media can be altered by adsorption of polar compounds and/or the deposition of organic material [Powers and Tambin, 1995; Demond et al., 1994]. Brown and Fatt [1956], Iwankow [1960], and Gimatudinov [1963] suggested that fractional wettability, that is, when both water-wet and oil-wet sites are present, may be found in many media.

The previously stated assumption, that the intermediate fluid forms a continuous layer between the wetting and nonwetting phases, may also be violated. Bradford and Leij [1995a, b] measured three-fluid  $P_c$ - $S$  relations in oil-wet and fractional wettability media, respectively, and observed that air-water, air-oil, and oil-water interfaces occurred due to the absence of a continuous intermediate layer. The capillary pressures at these interfaces cannot readily be predicted with existing methods. Lenhard and Bradford [1993] also measured three-fluid  $P_c$ - $S$  curves for strongly water-wet media and a nonspreading intermediate organic fluid; they found that the three-fluid air-oil  $P_c$ - $S$  curve could not be accurately predicted from the two-fluid air-oil  $P_c$ - $S$  curve.

In view of the above there is a need to develop approaches for predicting and modeling two-fluid and three-fluid  $P_c$ - $S$  relations when the solid is not exclusively wetted by one fluid, and/or the intermediate fluid is discontinuous. This paper presents a first attempt at predicting the  $P_c$ - $S$  relations for media with fractional wettability. Experimental  $P_c$ - $S$  relations, which were measured and discussed by Bradford and Leij [1995a, b], will be used for this purpose.

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### Fractional Wettability

The wettability of a solid surface is typically characterized by the contact angle ( $\phi$ ), which can be determined from a horizontal force balance at the three-phase contact line between a lighter fluid ( $l$ ), a drop of a denser fluid ( $d$ ), and a flat solid surface ( $s$ ). Young's equation states that

$$\cos(\phi_{sid}) = \frac{\sigma_{sl} - \sigma_{sd}}{\sigma_{ld}} \quad (1)$$

where  $\sigma$  is the interfacial tension (in newtons per meter) and the subscripts indicate the phases. The denser fluid wets the solid surface for  $\phi_{sid} < 90^\circ$ , while the lighter fluid wets the solid surface for  $\phi_{sid} > 90^\circ$ . Different contact angles may occur when the wetting fluid is advancing ( $\phi_{sid}^A$ ) or receding ( $\phi_{sid}^R$ ) (raindrop effect). Wetting and nonwetting fluids will be denoted by "W" and "N," respectively. In porous media with fractional wettability, the contact angle is obviously position-dependent, and any (macroscopic) value for the contact angle will constitute an effective parameter.

In a three-fluid medium of uniform wettability, either water ( $w$ ) or oil ( $o$ ) wets the solid, with the other liquid being the intermediate wetting fluid ( $l$ ). Air ( $a$ ) is always the nonwetting fluid. The coefficient of spreading for a drop of an intermediate fluid on a wetting fluid is defined as [Adamson, 1990, p. 110]:

$$\Sigma_{l/w} = \sigma_{NW} - (\sigma_{NI} + \sigma_{IW}) \quad (2)$$

A negative value for  $\Sigma_{l/w}$  indicates that the intermediate fluid does not spread on the wetting fluid, while a positive value indicates a tendency for spreading of the intermediate fluid. Generally,  $\Sigma_{o/w}$  is positive and  $\Sigma_{w/o}$  is negative, since  $\sigma_{aw} > \sigma_{ao}$  for most organic liquids. Note that the concepts of spreading of an intermediate fluid and wettability of the solid are similar. Fractional wettability hinders the formation of a continuous intermediate phase since oil and water may act as the intermediate fluids near water-wet and oil-wet surfaces, respectively. A continuous intermediate water layer is even less likely in view of the negative  $\Sigma_{w/o}$ .

The capillary pressure is defined as the drop in pressure over the curved interface between the nonwetting and wetting fluids. For a cylindrical capillary tube placed in a two-fluid system, the difference between the wetting and nonwetting fluids follows from the Laplace equation of capillarity [Adamson, 1990, p. 12]:

$$P_c = P_N - P_W = \frac{2\sigma_{NW}}{R} \cos(\phi_{sNW}) \quad (3)$$

where  $R$  is the radius of a capillary tube and  $\phi_{sNW}$  is the contact angle ( $\phi_{sNW} = \phi_{sid}$  for  $\phi_{sid} < 90^\circ$ ;  $\phi_{sNW} = 180^\circ - \phi_{sid}$  for  $\phi_{sid} > 90^\circ$ ). In oil-water systems the capillary pressure should actually be defined as  $P_{ow} = P_o - P_w$  for a water-wet system, and as  $P_{wo} = P_w - P_o$  for an oil-wet system. Since this capillary pressure definition is ambiguous and impractical for fractional wettability systems, we use  $P_c = P_{ow}$  with respect to water as the reference wetting phase. Hence  $P_{ow} > 0$  for  $\phi_{sow} < 90^\circ$ , and  $P_{ow} < 0$  for  $\phi_{sow} > 90^\circ$ .

In three-fluid water-wet media, where oils spread to form a continuous intermediate layer [McBride et al., 1992], capillary pressure drops occur over the oil-water and air-oil interfaces. In this case  $P_{ow}$  and  $P_{ao}$  have been found to be unique func-

**Table 1.** Summary of the Dependency of Three-Fluid Capillary Pressures on Liquid Saturations for Different Wettabilities of the Porous Medium

$P_c$	Water Wet	Oil Wet	Fractional Wettability
$P_{ow}$	$S_w^{aow}$	$S_w^{aow}$	$S_w^{aow}$
$P_{ao}$	$S_w^{aow}, S_o^{aow}$	$S_w^{aow}, S_o^{aow}$	$S_w^{aow}, S_o^{aow}$
$P_{aw}$	N/A	$S_w^{aow}, S_o^{aow}$	$S_w^{aow}, S_o^{aow}$

\*Capillary pressure depends to a lesser extent on this saturation.

†Capillary pressure depends mainly on this saturation.

tions of  $S_w^{aow}$  and  $S_o^{aow}$  (equal to  $S_w^{aow} + S_o^{aow}$ ), respectively [Lenhard and Parker, 1988; Ferrand et al., 1990; Bradford and Leij, 1995a]. The following conventions are used for the notation of fluid saturations: (1) the subscript denotes the fluid to which the saturation, which is expressed as volume of fluid per unit pore volume, pertains; and (2) superscripts denote all fluid phases present in the medium. Oil-wet and fractional wettability media often do not have a continuous intermediate oil phase. Consequently, capillary pressure drops may occur over air-water, air-oil, and oil-water interfaces. Bradford and Leij [1995a, b] found for oil-wet and fractional wettability media that  $P_{ow}$  depended on  $S_w^{aow}$ ,  $P_{ao}$  mainly depended on  $S_o^{aow}$  and to a lesser extent on  $S_w^{aow}$ , and  $P_{aw}$  mainly depended on  $S_w^{aow}$  and to a lesser extent on  $S_o^{aow}$ . Table 1 summarizes the saturation dependence of the three-fluid capillary pressures for the various medium wettabilities.

### Materials and Methods

The porous medium used in our experiments [Bradford and Leij, 1995a, b] consisted of several blasting sands (Corona Industrial Sand Company, Corona, California) containing 12.6% each of ASTM sieve sizes #12 and #16, 25.2% each of sizes #20 and #30, and 8.2% each of sizes #60, #70, and #90. This distribution corresponds to 25% very coarse sand, 50% coarse/medium sand, and 25% fine sand, according to the U.S. Department of Agriculture (USDA) textural classification [Soil Survey Staff, 1975]. Hydrophobic media were obtained by adding the blasting sands to a 5% solution of octadecyltrichlorosilane (OTS) in ethanol, followed by mixing in a shaker for 5 hours, after which the sands were air dried [Anderson et al., 1991]. Fractional wettability media were obtained by combining untreated and OTS-treated blasting sands using 0, 25, 50, 75, and 100% OTS sand. The untreated sands were strongly water-wet, while the OTS treated sands were oil-wet in oil-water systems and water repellent in air-water systems.

The oil used for the experiments was Soltrol 220 (Phillips Petroleum Company, Bartlesville, Oklahoma), which is composed of  $C_{13}$ - $C_{17}$  hydrocarbons, with a fluid density of  $\rho_o = 0.8 \text{ g/cm}^3$ . The fluid interfacial tensions, measured with a du Noüy ring [du Noüy, 1919], were  $\sigma_{aw} = 0.072 \text{ N/m}$ ,  $\sigma_{ao} = 0.024 \text{ N/m}$ , and  $\sigma_{ow} = 0.026 \text{ N/m}$ . When the water was contaminated by soltrol, we determined the interfacial tension for the air-water system,  $\sigma_{aw}^*$ , to be  $0.052 \text{ N/m}$ . The coefficients of spreading calculated according to (2), using  $\sigma_{aw} = 0.072 \text{ N/m}$ , were  $\Sigma_{o/w} = 0.022 \text{ N/m}$  and  $\Sigma_{w/o} = -0.074 \text{ N/m}$ . Similarly, the contaminated coefficients of spreading, calculated with  $\sigma_{aw}^* = 0.052 \text{ N/m}$ , were  $\Sigma_{o/w}^* = 0.002 \text{ N/m}$  and  $\Sigma_{w/o}^* = -0.054 \text{ N/m}$ .

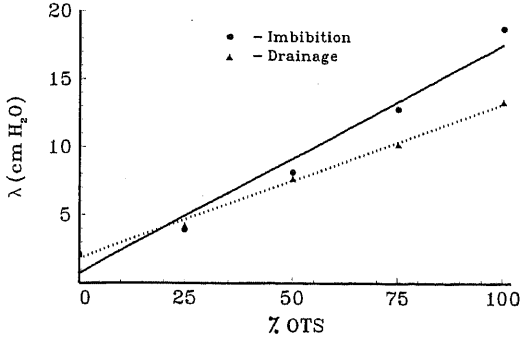


Figure 1. Relationship between  $\lambda$  and the fraction of oil-wet sand (percent OTS). The parameter  $\lambda$  was obtained by fitting (4) to measured  $P_{ao}-\bar{S}_o^{ao}$  and  $P_{ow}-\bar{S}_w^{ow}$  data during drainage and imbibition.

### Predicting $P_c$ - $S$ Relations for Two-Fluid Media

The measurement of air-liquid  $P_c$ - $S$  data is relatively easy. For uniformly wetted media the  $P_{ow}$ - $S_w^{ow}$  relation can be estimated by scaling the air-liquid  $P_c$ - $S$  data using the ratio of interfacial tensions [Lenhard and Parker, 1987] or the ratio of interfacial tensions and contact angles [Demond and Roberts, 1991; Bradford and Leij, 1995a]. This approach is less applicable for fractional wettability media where  $P_{ow}$  can be positive or negative and the contact angle is actually a function of saturation [Bradford and Leij, 1995b]. The scaling approach was therefore modified to account for fractional wettability according to

$$P_{ow}(\bar{S}_w^{ow}) = \frac{\sigma_{ow}}{\sigma_{ao}} P_{ao}(\bar{S}_o^{ao}) - \lambda \quad (4)$$

where  $\bar{S}_w^{ow} = (S_w^{ow} - S_{rw}^{ow}) / (1 - S_{rw}^{ow} - S_o^{ow})$ ,  $\bar{S}_o^{ao} = (S_o^{ao} - S_{ro}^{ao}) / (1 - S_{ro}^{ao} - S_{ra}^{ao})$ , and  $r$  denotes a residual value. The  $P_{ao}$ - $S_o^{ao}$  data describes the shape (pore size distribution) of the predicted  $P_{ow}$ - $S_w^{ow}$  relation, while the values of  $\sigma_{ow}/\sigma_{ao}$  and  $\lambda$  account for differences in interfacial tension and wetting properties, respectively. The shifting parameter,  $\lambda$ , allows for positive and negative predictions of  $P_{ow}$  from exclusively positive  $P_{ao}$  values without affecting the shape of the capillary pressure curve. This hypothesis is consistent with the observations of Fatt and Klikoff [1959] and Bradford and Leij [1995b].

An advantage of using (4) to predict  $P_{ow}$ - $S_w^{ow}$  from  $P_{ao}$ - $S_o^{ao}$  instead of  $P_{aw}$ - $S_w^{aw}$  data, is that the  $P_{ao}$ - $S_o^{ao}$  relationship can be measured over a significantly smaller range of pressures;  $\sigma_{ao} < \sigma_{aw}$  and hence  $P_{ao} < P_{aw}$  for a given saturation. Furthermore, according to (1)  $\sigma_{aw} > \sigma_{ao}$  leads to  $\phi_{saw} > \phi_{sao}$ . The value of  $\sigma_{ao}$  is also less susceptible to contamination and is therefore relatively constant, in contrast to  $\sigma_{aw}$  [Laliberte et al., 1966].

The relationship between  $\lambda$  and the hydrophobicity/wettability (i.e., the OTS percent) is shown in Figure 1. Values for  $\lambda$  were obtained according to the nonlinear least squares method of Marquardt [1963] by using (4) to describe the measured  $P_{ow}$ - $S_w^{ow}$  and  $P_{ao}$ - $S_o^{ao}$  data [Bradford and Leij, 1995b] for the main drainage and imbibition cycles. The relationships between  $\lambda$  and the fraction of oil-wet sand (percent OTS) during drainage ( $D$ ) and imbibition ( $I$ ), as obtained through linear regression, were

$$\lambda^D = 0.1135 \cdot \%OTS + 1.81 \quad (r^2 = 0.994) \quad (5)$$

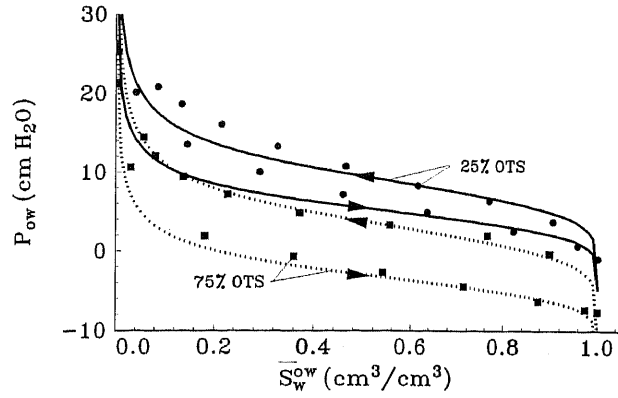


Figure 2. Predicted and measured  $P_{ow}$ - $S_w^{ow}$  relations for the 25 and 75% OTS media.

$$\lambda^I = 0.1680 \cdot \%OTS + 0.72 \quad (r^2 = 0.958) \quad (6)$$

Note that the difference in  $\lambda^D$  and  $\lambda^I$  increases as the OTS percent increases. An increase in hysteresis of the  $P_{ow}$ - $S_w^{ow}$  curve with the OTS fraction. Figure 2 shows a comparison of calculated and measured  $P_{ow}$ - $S_w^{ow}$  relations, during main drainage and imbibition of water, for the 25 and 75% OTS media. The calculated  $P_{ow}$ - $S_w^{ow}$  curves were obtained from measured  $P_{ao}$ - $S_o^{ao}$  data according to (4), using (5) and (6) to predict  $\lambda$ . The observed and calculated data agree fairly well.

We postulate that the expressions for  $\lambda$  as a function of the oil-wet sand fraction, as developed for "medium 1," can be extended to other oils and media for which we want to predict the  $P_{ow}$ - $S_w^{ow}$  relation from  $P_{ao}$ - $S_o^{ao}$  data, assuming that for the second system ("medium 2") we also have  $\phi_{sao} = 0^\circ$ . Equation (3) can be used to relate any value of the  $P_{ow}$ - $S_w^{ow}$  curve for the "known" medium 1 to a point on the curve for the "unknown" medium 2 according to

$$P_{ow2}(\bar{S}_w^{ow}) = P_{ow1}(\bar{S}_w^{ow}) \cdot \frac{R_1 \sigma_{ow2} \cos[\phi_{sow2}(\bar{S}_w^{ow})]}{R_2 \sigma_{ow1} \cos[\phi_{sow1}(\bar{S}_w^{ow})]} \quad (7)$$

where the subscripts 1 and 2 indicate the two media. We assume that the saturation-dependent effective oil-water contact angles are the same for both media for a given "equivalent" OTS percent. Furthermore, we estimate the ratio of  $R_1/R_2$ , which characterizes the pore radii of pores in both media that are just being filled with water/oil at a certain saturation, from the radii of an equivalent capillary tube just being imbibed/drained in the center of the saturation range. Application of (3) to air-oil data (i.e.,  $\bar{S}_o^{ao} = 0.5$ ) gives

$$\frac{R_1}{R_2} = \frac{\sigma_{ao1} P_{ao2}(0.5)}{\sigma_{ao2} P_{ao1}(0.5)} \quad (8)$$

Substitution of (8) into (7) yields

$$P_{ow2}(\bar{S}_w^{ow}) = P_{ow1}(\bar{S}_w^{ow}) \cdot \frac{\sigma_{ow2} \sigma_{ao1} P_{ao2}(0.5)}{\sigma_{ow1} \sigma_{ao2} P_{ao1}(0.5)} \quad (9)$$

An expression for  $\lambda_2$  can now be found by relating  $P_{ow1}$  and  $P_{ow2}$  in (9) according to (4), where the value of  $\lambda_1$  is already given by the empirical expressions shown in (5) and (6). After some rearranging, we find the desired expression for  $\lambda_2$  as

$$\lambda_2^D = \frac{\sigma_{ow2} \cdot P_{ao2}(0.5)}{\sigma_{ao2} \cdot 15.17} [0.1135 \cdot \%OTS + 1.81] \quad (10)$$

$$\lambda_2^I = \frac{\sigma_{ow2} \cdot P_{ao2}(0.5)}{\sigma_{ao2} \cdot 11.02} [0.1680 \cdot \%OTS + 0.72] \quad (11)$$

The constants 15.17 and 11.02 are the values of  $\sigma_{ow1} P_{ao1}(0.5) / \sigma_{ao1}$  for which (5) and (6) were obtained, respectively. Note that (10) and (11) scale  $\lambda_1$  by  $\sigma_{ow2} \sigma_{ao1} / \sigma_{ow1} \sigma_{ao2}$  to account for differences in fluid properties and by  $P_{ao2}(0.5) / P_{ao1}(0.5)$  for differences in pore size.

The above prediction of the  $P_{ow} - \bar{S}_w^{ow}$  relation, according to (4) with  $\lambda$  defined by (10) and (11), requires measured  $P_{ao} - \bar{S}_o^{ao}$  data and knowledge of the "equivalent OTS fraction," that is, oil-wet fraction. The  $P_{ao} - \bar{S}_o^{ao}$  relation was measured for various media by Laliberte *et al.* [1966], among others. It is possible to derive relationships between the OTS fraction and the United States Bureau of Mines [Donaldson *et al.*, 1969] and the Amott-Harvey [Boneau and Clampitt, 1977] wettability indices. Such relationships can be used to estimate "equivalent OTS fraction" from a measured wettability index. Other methods to estimate the oil-wet fraction of a medium warrant further investigation, for example, investigation based on knowledge of the organic matter content or wetting characteristics of the mineral.

## $P_c$ -S Relations for Three-Fluid Media

### Predictive Methods

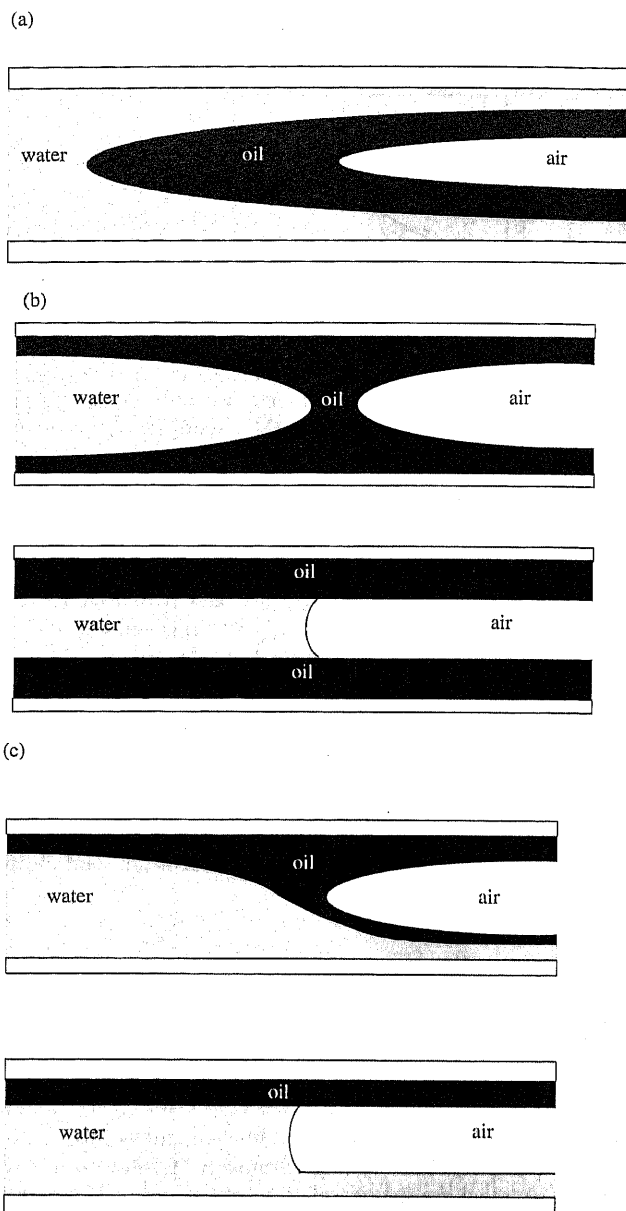
Figures 3a, 3b, and 3c show hypothetical distributions of air, oil, and water in water-wet (Figure 3a), oil-wet (Figure 3b), and fractional wettability (Figure 3c) pores. Note that there are two capillary pressure drops for the water-wet medium (Figure 3a), since oil spreads well on water, while two scenarios are plausible for oil-wet and fractional wettability media (Figures 3b and 3c), since water does not spread on the air-oil interface. The bottom panels of Figures 3b and 3c show the scenario with a maximum of three pressure drops. For greater  $S_o^{aow}$  the scenarios in the top panels are the most likely, while for greater  $S_w^{aow}$ , in contrast, the scenarios in the bottom panels may be more representative.

Note in Table 1 that regardless of the wettability of the medium,  $P_{ow}$  is exclusively a function of  $S_w^{aow}$ . Changes in  $S_w^{aow}$  (for a constant  $S_o^{aow}$ ) lead to complementary changes in  $S_a^{aow}$ . These changes in  $S_a^{aow}$  will alter the oil-water interface for the various media wettabilities, making  $P_{ow}$  dependent upon  $S_w^{aow}$ . In contrast, changes in  $S_o^{aow}$  (for a constant  $S_w^{aow}$  with complementary changes in  $S_a^{aow}$ ) will alter primarily the air-oil interface ( $P_{ao}$ ); the oil-water interface is now largely unchanged, and thus  $P_{ow}$  is not much affected by  $S_o^{aow}$ . Since  $P_{ow}$  is a function of the water saturation for both two-fluid and three-fluid media, we hypothesize that the fractional wettability  $P_{ow} - S_w^{aow}$  curve can be predicted from  $P_{ow} - S_w^{aow}$  data analogous to Leverett's approach [Leverett, 1941] for a water-wet medium as

$$P_{ow}(\bar{S}_w^{aow}) = P_{ow}(\bar{S}_w^{ow}) \quad (12)$$

where  $\bar{S}_w^{ow}$  is defined as in (4), and  $\bar{S}_w^{aow} = (S_w^{aow} - S_{rtl}^{aow}) / (1 - S_{rtl}^{aow} - S_{ra}^{aow})$ , in which the subscripts  $r$  and  $tl$  denote a residual value and the total liquid saturation ( $S_{tl}^{aow} = S_w^{aow} + S_o^{aow}$ ), respectively. In contrast to the standard application of Leverett's assumption, (12) allows for positive and negative values of  $P_{ow}$ ; water is mainly the wetting fluid for  $P_{ow} > 0$  and mainly the intermediate fluid for  $P_{ow} < 0$ .

As previously mentioned, Table 1 indicates that for a frac-



**Figure 3.** Hypothetical three-fluid distributions in (a) water-wet, (b) oil-wet, and (c) fractional wettability pores.

tional wettability medium a change in  $S_o^{aow}$  (at a constant  $S_w^{aow}$ ) primarily affects the air-oil interface ( $P_{ao}$ ) while the oil-water interface ( $P_{ow}$ ) is largely unchanged. This result has been attributed to discontinuity of the intermediate fluid and the similar spreading behavior of oil as a wetting ( $\phi_{sao}^A = 0^\circ$  and  $\phi_{sao}^R = 0^\circ$ ) or an intermediate ( $\Sigma_{o/w}^* = +0.002$  N/m) fluid [Bradford and Leij, 1995b]. We refer below to  $S_{tl}^{aow}$  as  $S_{tl(o)}^{aow}$  when  $S_o^{aow}$  is changed at a constant  $S_w^{aow}$ , while the residual air saturation,  $S_{ra}^{aow}$ , will be denoted as  $S_{ra(o)}^{aow}$ . The value of  $P_{ao}$  in two-fluid and three-fluid media reflects similar changes in the air-oil interface as a result of changes in  $S_o^{aow}$  and  $S_{tl(o)}^{aow}$ , respectively. We therefore hypothesize, analogous to Leverett's approach, that the  $P_{ao} - S_o^{aow}$  data can be used to predict the  $P_{ao} - S_{tl(o)}^{aow}$  curve according to

$$P_{ao}(\bar{S}_{tl(o)}^{aow}) = P_{ao}(\bar{S}_o^{ao}) \quad (13)$$

where  $\bar{S}_{tl(o)}^{aow} = (S_{tl}^{aow} - S_{rtl}^{aow}) / (1 - S_{rtl}^{aow} - S_{ra(o)}^{aow})$ .

For fractional wettability media, Table 1 indicates that a change in water saturation (at a constant  $S_o^{aow}$ ) will affect  $P_{ao}$  to a lesser extent than changes in  $S_o^{aow}$  (or  $S_{il(o)}^{aow}$ ) will. Consequently, when  $S_w^{aow}$  changes (at a constant  $S_o^{aow}$ ) the  $P_{ao}$ - $\bar{S}_{il(w)}^{aow}$  relation cannot be obtained from two-fluid  $P_{ao}$ - $S_o^{aow}$  data according to (13). We will denote  $S_{il}^{aow}$  as  $S_{il(w)}^{aow}$  when  $S_w^{aow}$  is changed at a constant  $S_o^{aow}$ , while the residual air saturation,  $S_{ra}^{aow}$ , will be denoted as  $S_{ra(w)}^{aow}$ . The  $P_{ao}$ - $\bar{S}_{il(w)}^{aow}$  relation is more difficult to predict than  $P_{ao}$ - $\bar{S}_{il(o)}^{aow}$  due to the manner in which  $P_{ao}$  is affected by changes in  $S_w^{aow}$  (cf. two different scenarios in Figures 3b and 3c). We postulate that the  $P_{ao}$ - $\bar{S}_{il(w)}^{aow}$  relationship can be predicted from two-fluid data by using an empirical correction for the  $P_{ao}$ - $S_o^{aow}$  data. *Bradford and Leij* [1995b] observed that the  $P_{ao}$ - $\bar{S}_{il(w)}^{aow}$  relation was mostly linear during drainage and imbibition for  $S_{rl}^{aow} < \bar{S}_{il(w)}^{aow} < 1$ . We therefore approximate the  $P_{ao}$ - $\bar{S}_{il(w)}^{aow}$  relation by linearly adjusting the  $P_{ao}$ - $S_o^{aow}$  data according to

$$P_{ao}(\bar{S}_{il(w)}^{aow}) = P_{ao}(\bar{S}_o^{aow}) + A \cdot [\bar{S}_{il(w)}^{aow} - \bar{S}_o^{aow}] \quad (14)$$

where  $A$  (centimeters of water) is the slope of the  $P_{ao}$ - $\bar{S}_{il(w)}^{aow}$  curve at constant  $\bar{S}_o^{aow}$ . Note that according to (13) and (14), the value of  $P_{ao}$  at a given  $\bar{S}_{il}^{aow}$  depends on whether  $S_w^{aow}$  or  $S_o^{aow}$  was previously varied. Consequently, a discontinuity in  $P_{ao}$  may occur at the "reversal point" where  $P_{ao}$ - $\bar{S}_{il(w)}^{aow}$  changes to  $P_{ao}$ - $\bar{S}_{il(o)}^{aow}$ .

The slope,  $A$ , of the  $P_{ao}$ - $\bar{S}_{il(w)}^{aow}$  curve for fractional wettability media is not known a priori. An estimate of  $A$  may be obtained from  $P_{ao}$ - $\bar{S}_{il(w)}^{aow}$  relations during drainage and imbibition for  $\bar{S}_{rl}^{aow} < \bar{S}_{il(w)}^{aow} < 1$  using the linear regression equation:

$$P_{ao}(\bar{S}_{il(w)}^{aow}) = A \cdot \bar{S}_{il(w)}^{aow} + B \quad (15)$$

where  $B$  is the intercept (centimeters of water). The following relationship between  $A$  and percent of OTS was established by a second linear regression:

$$A^D = 0.068 \cdot \%OTS - 7.52 \quad (r^2 = 0.739) \quad (16)$$

$$A^I = 0.013 \cdot \%OTS - 6.60 \quad (r^2 = 0.203) \quad (17)$$

The prediction of  $P_{ao}$  in this manner during water imbibition is poorer than during water drainage. This result is likely due to the formation of air-water interfaces (located near oil-wet solids) through which water displaces air. Figures 3b and 3c show that when few air-water interfaces are present (top panels' scenario), an increasing  $S_w^{aow}$  may affect  $P_{ao}$ . After an air-water interface has formed (bottom panels' scenario) air can readily exit without significantly affecting  $P_{ao}$ .

Finally, the  $P_{aw}$ - $\bar{S}_{il}^{aow}$  relation needs to be predicted for fractional wettability media since air-water interfaces exist. The prediction of the  $P_{aw}$ - $\bar{S}_{il}^{aow}$  relation from  $P_{aw}$ - $\bar{S}_w^{aow}$  data was not successful, since water wets the solid well ( $\phi_{sow}^A = 51.6^\circ$  and  $\phi_{sow}^R = 0^\circ$ ) but spreads poorly on oil if water is the intermediate fluid ( $\Sigma_{w/o}^* = -0.054$  N/m). Alternatively, the  $P_{aw}$ - $\bar{S}_{il}^{aow}$  curve can be obtained from the following constraints on the three-fluid capillary pressures and saturations:

$$P_{aw}(\bar{S}_{il}^{aow}) = P_{ow}(\bar{S}_w^{aow}) + P_{ao}(\bar{S}_{il}^{aow}) \quad (18)$$

Note that (18) applies since both the water and oil pressures are measured with respect to atmospheric pressure. When the  $P_{ow}(\bar{S}_w^{aow})$  and  $P_{ao}(\bar{S}_{il}^{aow})$  relations are predicted from the two-fluid  $P_c$ - $S$  curves according to (12) and (13),  $P_{aw}(\bar{S}_{il}^{aow})$  can be given as

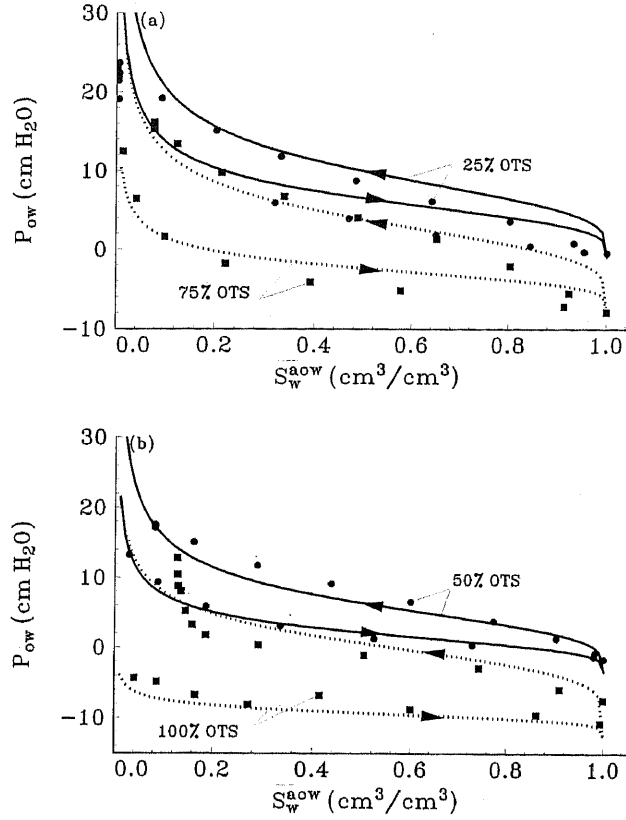


Figure 4. Observed  $P_{ow}$ - $\bar{S}_w^{aow}$  data and curves predicted according to (21) for (a) 25 and 75% OTS and (b) 50 and 100% OTS.

$$P_{aw}(\bar{S}_{il(w)}^{aow}) = P_{ow}(\bar{S}_w^{aow}) + P_{ao}(\bar{S}_o^{aow}) \quad (19)$$

The  $P_{aw}$ - $\bar{S}_{il(w)}^{aow}$  relation can similarly be predicted from (12) and (14) as

$$P_{aw}(\bar{S}_{il(w)}^{aow}) = P_{ow}(\bar{S}_w^{aow}) + P_{ao}(\bar{S}_o^{aow}) + A(\bar{S}_{il(w)}^{aow} - \bar{S}_o^{aow}) \quad (20)$$

### Applications

The  $P_{ow}$ - $\bar{S}_w^{aow}$  relationship, as predicted from the measured  $P_{ow}$ - $\bar{S}_w^{aow}$  data according to (12), was described with the modified van Genuchten  $P_c$ - $S$  model [*Bradford and Leij*, 1995b] as

$$P_{ow}(\bar{S}_w^{aow}) = \frac{1}{\alpha_{ow}} [\bar{S}_w^{aow-1/n_{ow}} - 1]^{1/n_{ow}} - \lambda \quad (21)$$

where  $\alpha_{ow}$  and  $n_{ow}$  are obtained by fitting (21) to measured  $P_{ow}$ - $\bar{S}_w^{aow}$  data ( $m_{ow} = 1 - 1/n_{ow}$ ). The value of  $\lambda$  is set equal to the magnitude of the lowest  $P_{ow}$  value of the two-fluid curve to ensure that  $(P_{ow} + \lambda) \geq 0$  [cf. *Powers and Tambin*, 1995]. Observed  $P_{ow}$ - $\bar{S}_w^{aow}$  data, as well as the curves predicted according to (21), are shown for the 25 and 75% OTS in Figure 4a and for 50 and 100% OTS in Figure 4b. The "measured" values of  $S_{rw}^{aow}$ ,  $S_{roa}^{aow} = S_{ro}^{aow} + S_{ra}^{aow}$ , and  $\lambda$  as well as the fitted values of  $\alpha_{ow}^I$ ,  $\alpha_{ow}^D$ , and  $n_{ow}$  are given in Table 2. The estimates for  $S_{rw}^{aow}$  and  $S_{roa}^{aow}$  correspond to the minimum and maximum ( $S_{roa}^{aow} = 1 - S_w^{aow}$ ) water saturations, respectively, attained during the experiments. Figure 4 indicates a reasonable agreement between the observed and predicted  $P_{ow}$ - $\bar{S}_w^{aow}$  curves, indicating that (12) is appropriate to predict the  $P_{ow}$ - $\bar{S}_w^{aow}$  curve from  $P_{ow}$ - $\bar{S}_w^{aow}$  data for fractional wettability me-

**Table 2.** Values of  $S_{rw}^{aow}$ ,  $S_{roa}^{aow}$ ,  $\lambda$ ,  $\alpha_{ow}^I$ ,  $\alpha_{ow}^D$ , and  $n_{ow}$  Employed in (21) to Predict the  $P_{ow}-\bar{S}_w^{aow}$  Curves

Percent OTS	$S_{rw}^{aow}$	$S_{roa}^{aow}$	$\lambda$ , cm	$\alpha_{ow}^I$ , cm <sup>-1</sup>	$\alpha_{ow}^D$ , cm <sup>-1</sup>	$n_{ow}$
25	0.39	0.12	0.93	0.15	0.10	3.82
50	0.28	0.22	3.34	0.20	0.12	3.85
75	0.25	0.14	7.64	0.21	0.09	4.50
100	0.26	0.21	12.78	0.30	0.08	5.64

dia. Notice in Table 2 that the values of  $\lambda$  and  $n_{ow}$  increase with increasing OTS fraction; this reflects a lower  $P_{ow}$  value and an increasing slope at the inflection point of the  $P_{ow}-\bar{S}_w^{aow}$  curve, respectively. The values of  $\alpha_{ow}^I$  and  $\alpha_{ow}^D$  are related to  $\lambda$  since  $\alpha_{ow}$  characterizes the "entry pressure" of the ( $P_{ow} + \lambda$ ) -  $\bar{S}_w^{aow}$  curve.

The  $P_{ow}-\bar{S}_w^{aow}$  relation may alternatively be predicted from  $P_{ao}-\bar{S}_o^{aoo}$  data when the previously discussed scaling and shifting approach according to (4) is first used to predict the  $P_{ow}-\bar{S}_w^{aow}$  relation. The three-fluid  $P_{ow}-\bar{S}_w^{aow}$  curve is predicted subsequently with (12):

$$P_{ow}(\bar{S}_w^{aow}) = \frac{\sigma_{ow}}{\sigma_{ao}\alpha_{ao}} [\bar{S}_o^{aoo-1/n_{ao}} - 1]^{1/n_{ao}} - \lambda \quad (22)$$

where the values of  $\alpha_{ao}^D = 0.08$ ,  $\alpha_{ao}^I = 0.11$ , and  $n_{ao} = 5.80$  ( $m_{ao} = 1 - 1/n_{ao}$ ) were obtained by fitting the  $P_c-S$  model of *van Genuchten* [1980] to  $P_{ao}-\bar{S}_o^{aoo}$  data. The values for  $\lambda$  were obtained from (5) and (6). Figure 5 shows the  $P_{ow}-\bar{S}_w^{aow}$  data for 25 and 75% OTS (Figure 5a), and 50 and 100% OTS

(Figure 5b) as well as the predicted curves according to (22). The measured values of  $S_{rw}^{aow}$  and  $S_{roa}^{aow}$  were given earlier, in Table 2. Both (21) and (22) appear to be viable means for predicting the  $P_{ow}-\bar{S}_w^{aow}$  curves from two-fluid  $P_c-S$  relations.

The  $P_{ao}-\bar{S}_{il(o)}^{aoo}$  curve, as predicted from  $P_{ao}-\bar{S}_o^{aoo}$  data according to (13), can be described with the  $P_c-S$  model of *van Genuchten* [1980]:

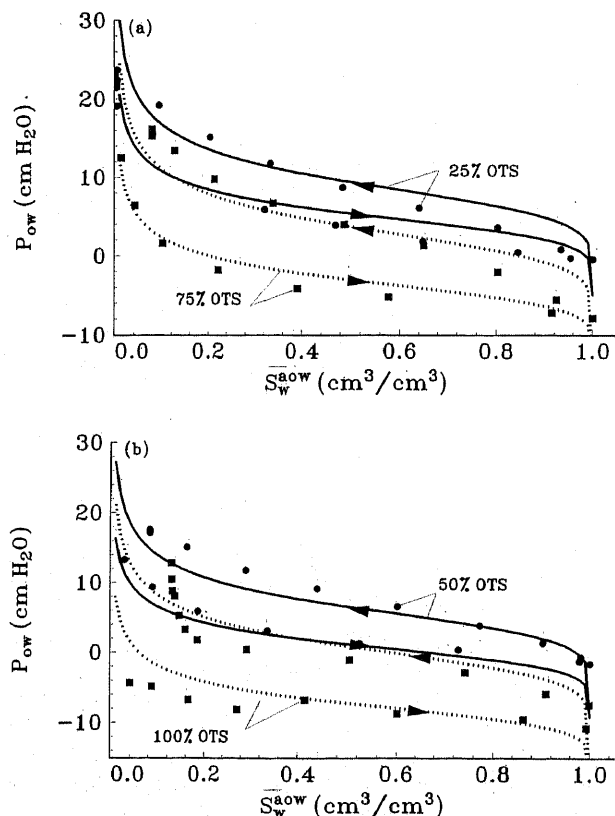
$$P_{ao}(\bar{S}_{il(o)}^{aoo}) = \frac{1}{\alpha_{ao}} [\bar{S}_o^{aoo-1/n_{ao}} - 1]^{1/n_{ao}} \quad (23)$$

in which the previously given parameters  $\alpha_{ao}$  and  $n_{ao}$  were obtained by fitting (23) to measured  $P_{ao}-\bar{S}_o^{aoo}$  data. The estimation of a similar three-fluid curve for variable water saturation is a bit more involved, as noted earlier. The  $P_{ao}-\bar{S}_{il(w)}^{aow}$  relation is obtained according to (14) using (16) and (17) for determining  $A^D$  and  $A^I$ , respectively. Figure 6 shows the predicted and observed  $P_{ao}-\bar{S}_{il(o)}^{aoo}$  curves for the different OTS sand fractions. The predicted  $P_{ao}-\bar{S}_{il(o)}^{aoo}$  curves agree reasonably well with the experimental data, indicating that (13) may successfully describe the three-fluid  $P_{ao}-\bar{S}_{il(o)}^{aoo}$  relations. This result is likely due to the similar spreading behavior of oil as the wetting or intermediate fluid. In contrast, the predicted  $P_{ao}-\bar{S}_{il(w)}^{aow}$  curves do not describe the data as well, especially during water imbibition (cf. equation (17)). This lack of agreement was attributed to the manner in which an increase in  $S_w^{aow}$  initially influences  $P_{ao}$  until a sufficiently large air-water interface has developed (cf. top panels' scenario in Figures 3b and 3c). For a relatively large air-water interface, water can displace air without greatly affecting  $P_{ao}$ . In general, the difference between  $P_{ao}$  for  $\bar{S}_{il(o)}^{aoo}$  and for  $\bar{S}_{il(w)}^{aow}$  increases with the OTS fraction since more of the water acts as the intermediate fluid and therefore influences the air-oil interface ( $P_{ao}$ ) to a lesser extent. Table 3 contains values for the "measured"  $S_{ra(o)}^{aow}$  and  $S_{ra(w)}^{aow}$ , the predicted  $A^D$  and  $A^I$ , and the fitted  $S_{ril}^{aow}$ .

Notice in Table 3 that  $S_{ra(o)}^{aow}$  exceeds  $S_{ra(w)}^{aow}$  for all wettabilities, a result which may be explained by nonwetting fluid entrapment. *Chatzis et al.* [1983] stated that the main mechanism of nonwetting fluid entrapment is snap-off. Snap-off occurs in the center of a pore due to capillary instabilities at the pore throats when the amount of wetting/intermediate fluid supplied to the pore, moving along its surface, is increased. The coefficient of spreading for water on oil,  $\Sigma_{w/o}^* = -0.054$  N/m, suggests that water and air "similarly wet" the oil surface. In contrast, the coefficient of spreading of oil on water,  $\Sigma_{o/w}^* = +0.002$  N/m, suggests that oil strongly wets the water surface. It is likely that increasing  $S_o^{aow}$  leads to air entrapment by snap-off, while air entrapment occurs to a lesser extent when  $S_w^{aow}$  increases.

Table 3 also shows values for  $S_{ril}^{aow}$  obtained by fitting (22) to  $P_{ao}-\bar{S}_{il(o)}^{aoo}$  data using the nonlinear least squares method. Note that  $S_{ril}^{aow}$  was the only three-fluid parameter obtained by fitting to the two-fluid data. A measured value of  $S_{ril}^{aow}$  was not employed to determine  $\bar{S}_{il}^{aow}$  since the residual value of  $S_{il}^{aow}$  (which corresponds to the point on the  $P_{ao}-\bar{S}_{il}^{aow}$  curve where the oil and water phases become discontinuous) was not determined experimentally. The fitted value of  $S_{ril}^{aow}$  ( $= S_{rw}^{aow} + S_{roa}^{aow}$ ) is actually lower than the value of  $S_{rw}^{aow}$  shown in Table 2. The latter is merely the lowest  $S_w^{aow}$  attained during the experiments and does not represent the point on the  $P_{aw}-S_w^{aow}$  curve where the water phase becomes discontinuous.

The continuous description of the  $P_{aw}-S_{il}^{aow}$  relation follows directly from (19) and (20). Figure 7 shows the observed and



**Figure 5.** Observed  $P_{ow}-\bar{S}_w^{aow}$  data and curves predicted according to (22) for (a) 25 and 75% OTS and (b) 50 and 100% OTS.

**Table 3.** Values of  $S_{rl}^{aow}$ ,  $S_{ra(o)}^{aow}$ ,  $S_{ra(w)}^{aow}$ ,  $A^D$ , and  $A^I$  Used in (23) and (14) to Predict the  $P_{ao}-\bar{S}_{ll}^{aow}$  Curves

Percent OTS	$S_{rl}^{aow}$	$S_{ra(o)}^{aow}$	$S_{ra(w)}^{aow}$	$A^D$ , cm	$A^I$ , cm
25	0.40	0.07	0.00	-5.82	-6.28
50	0.18	0.13	0.09	-4.12	-5.95
75	0.23	0.11	0.03	-2.42	-5.63
100	0.29	0.11	0.06	-0.72	-5.30

predicted  $P_{aw}-\bar{S}_{ll}^{aow}$  relations for the various OTS fractions. The predicted  $P_{aw}-\bar{S}_{ll}^{aow}$  curves, obtained according to (19) and (20), describe the data reasonably well. This result is not surprising since the  $P_{ow}-\bar{S}_w^{aow}$  and  $P_{ao}-\bar{S}_o^{aow}$  data could reasonably predict the corresponding three-fluid  $P_c-S$  relations. The  $P_{aw}-\bar{S}_{ll}^{aow}$  relationship may also be obtained by using (22) instead of (21) to describe  $P_{ow}-\bar{S}_w^{aow}$  data in (19) and (20); the results for this approach are similar to those shown Figure 7. Note that if (21) is employed, any three-fluid  $P_c-S$  relation in media with fractional wettability can be predicted from  $P_{ao}-\bar{S}_o^{aow}$  data. As previously mentioned, the value of  $P_{ow}-\bar{S}_w^{aow}$  is constant in (19) for a variable  $\bar{S}_{ll(o)}^{aow}$ . Consequently, the observed and predicted  $P_{aw}-\bar{S}_{ll(o)}^{aow}$  relations may differ significantly at low water saturations, that is, when  $S_w^{aow}$  is near  $S_{rw}^{aow}$ ;  $P_{ow}$  changes greatly for a small change in  $S_w^{aow}$  in this part of the  $P_{ow}-S_w^{aow}$  curve. The value of  $S_{rw}^{aow}$  was therefore adjusted a few percent (<2%) so that the constant value of  $P_{ow}-\bar{S}_w^{aow}$  used in (19) better describes the observed  $P_{aw}-\bar{S}_{ll(o)}^{aow}$  data.

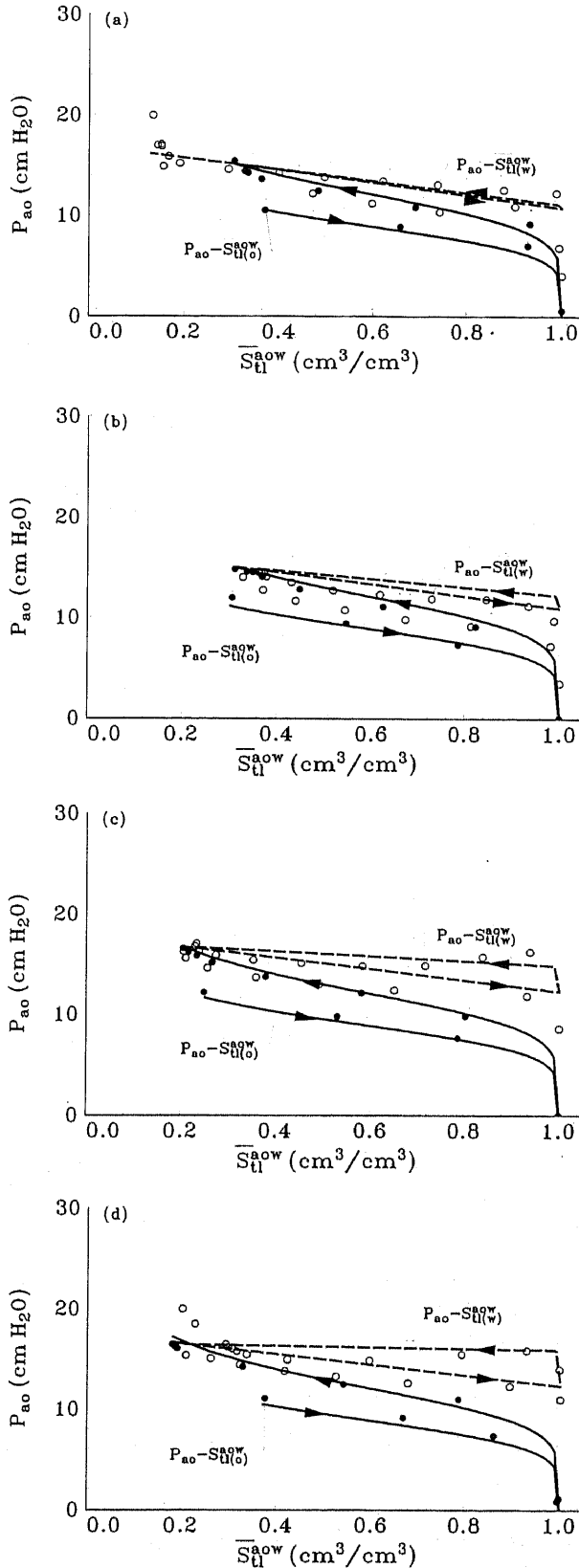
### Summary and Conclusions

Existing methods to predict and model two-fluid and three-fluid  $P_c-S$  relations for porous media with fractional wettability are generally inadequate. A comprehensive approach was outlined and applied for predicting and modeling two-fluid and three-fluid  $P_c-S$  relationships in case two liquids both act as the wetting fluid. Data for the air-oil (preferably) or air-water  $P_c-S$  curves in two-fluid media with fractional wettability serve as a starting point for the predictive method.

In fractional wettability media containing oil and water, the value of  $P_{ow}$  for a given  $S_w^{aow}$  may be positive or negative since both water-wet and oil-wet sites are present. In addition to scaling the  $P_{ao}-\bar{S}_o^{aow}$  relation using the ratio of interfacial tensions, a constant shifting parameter,  $\lambda$ , was used to predict positive and negative values for  $P_{ow}$  from exclusively positive  $P_{ao}$  values. Good agreement was observed between the calculated and observed  $P_{ow}-\bar{S}_w^{aow}$  relations for this approach. A regression relation was derived for the value of  $\lambda$  as a function of the fraction of oil-wet sand for the drainage and imbibition branches. These regression relations were extended to other media and fluids by characterizing the pore radii in both media with the radii of an equivalent capillary tube just being imbibed/drained to the center of the saturation range.

In fractional wettability media containing three fluids (i.e., air, water, and oil), three capillary pressures may occur:  $P_{ow}$ ,  $P_{ao}$ , and  $P_{aw}$ . We postulated that the  $P_{ow}-\bar{S}_w^{aow}$  relation could be estimated from the measured or predicted (using equation (4))  $P_{ow}-\bar{S}_w^{aow}$  data according to (12) since the value of  $P_{ow}$  is a function of the water saturation for both two-fluid and three-fluid media. A reasonable agreement between the observed and predicted  $P_{ow}-\bar{S}_w^{aow}$  curves was found.

We also hypothesized that the  $P_{ao}-\bar{S}_{ll(o)}^{aow}$  relation, that is,



**Figure 6.** Observed  $P_{ao}-\bar{S}_{ll}^{aow}$  data and curves predicted according to (14) for  $P_{ao}-\bar{S}_{ll(w)}^{aow}$  and according to (23) for  $P_{ao}-\bar{S}_{ll(o)}^{aow}$  for (a) 25% OTS, (b) 50% OTS, (c) 75% OTS, and (d) 100% OTS.

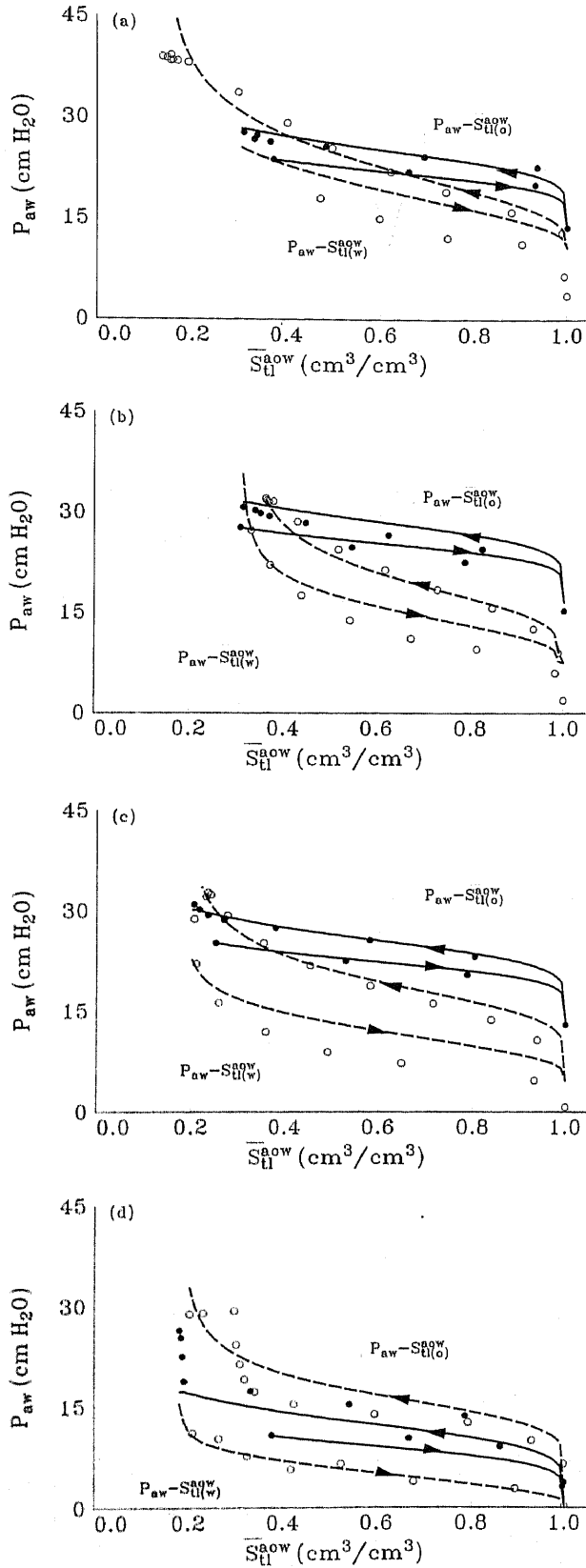


Figure 7. Observed  $P_{aw}-\bar{S}_{ll}^{aow}$  data and curves predicted according to (19) for  $P_{aw}-\bar{S}_{ll(o)}^{aow}$  and according to (20) for  $P_{aw}-\bar{S}_{ll(w)}^{aow}$  for (a) 25% OTS, (b) 50% OTS, (c) 75% OTS, and (d) 100% OTS.

air-oil pressure in three-fluid media with fixed water saturation, could be obtained according to (13) from the  $P_{ao}-\bar{S}_o^{ao}$  relation since the value of  $P_{ao}$  in two-fluid and three-fluid media reflects similar changes in the air-oil interface ( $P_{ao}$ ) with changes in  $S_o^{ao}$  and  $S_{il(o)}^{aow}$ , respectively. Observed and predicted  $P_{ao}-\bar{S}_{il(o)}^{aow}$  curves agreed fairly well. The  $P_{ao}-\bar{S}_{il(w)}^{aow}$  relation was predicted from empirically corrected  $P_{ao}-\bar{S}_o^{ao}$  data according to (14) since changes in  $S_{il(w)}^{aow}$  affected the air-oil interface ( $P_{ao}$ ) to a lesser extent than changes in  $S_{il(o)}^{aow}$ . Predicted and observed  $P_{ao}-\bar{S}_{il(w)}^{aow}$  relations did not agree as well as for the  $P_{ao}-\bar{S}_{il(o)}^{aow}$  relations due to the manner in which changes in  $S_w^{aow}$  influenced  $P_{ao}$ ; changes in  $S_w^{aow}$  may influence  $P_{ao}$  (scenario in upper panels in Figures 3b and 3c) until air-water interfaces form (scenario in lower panels in Figures 3b and 3c).

The  $P_{aw}-\bar{S}_{ll}^{aow}$  relation was obtained from the measured  $P_{ow}-\bar{S}_w^{aow}$  and  $P_{ao}-\bar{S}_o^{ao}$  relations using constraints attributable to the experimental procedure, according to (19) for changing  $\bar{S}_{il(o)}^{aow}$  and according to (20) for changing  $\bar{S}_{il(w)}^{aow}$ . A reasonable agreement was obtained between the observed and predicted  $P_{aw}-\bar{S}_{ll}^{aow}$  curves.

This paper presents a first attempt at predicting fractional wettability  $P_c-S$  relations. Our empirical approach involves linear regression of the oil-wet fraction of soils or the "equivalent" OTS percentage. If the OTS fraction is not known a priori, it can be estimated from wettability indices (e.g., U.S. Bureau of Mines and Amott-Harvey). Alternative methods to predict  $P_c-S$  curves may use other empirical or physicoempirical correlation models. Further research is also needed to estimate  $P_c-S$  data that were independently measured for both disturbed and undisturbed porous media with fractional wettability.

### Notation

- $a$  air.
- $A$  slope of  $P_{ao}-S_{il(w)}^{aow}$  curve.
- $d$  denser fluid.
- $D$  drainage.
- $I$  imbibition (superscript).
- $I$  intermediate wetting fluid (subscript).
- $l$  lighter fluid.
- $m$  parameter for van Genuchten  $P_c-S$  model ( $m = 1 - 1/n$ ).
- $n$  parameter (slope of inflection point) for van Genuchten  $P_c-S$  model.
- $N$  nonwetting fluid.
- $o$  oil.
- OTS octadecyltrichlorosilane.
- $P_c$  capillary pressure (N/m<sup>2</sup>, cm water).
- $P_{ij}$  capillary pressure drop over interface between fluids  $i$  and  $j$ , that is,  $P_i - P_j$  (N/m<sup>2</sup>, cm water).
- $R$  radius of a sphere or capillary tube (cm).
- $s$  solid.
- $S$  saturation (cm<sup>3</sup>/cm<sup>3</sup>).
- $S_i^{ij}$  saturation of fluid  $i$  in a medium containing the two fluids  $i$  and  $j$  (cm<sup>3</sup>/cm<sup>3</sup>).
- $S_i^{ijk}$  saturation of fluid  $i$  in a medium containing the three fluids  $i$ ,  $j$ , and  $k$  (cm<sup>3</sup>/cm<sup>3</sup>).
- $S_r$  residual saturation (cm<sup>3</sup>/cm<sup>3</sup>).
- $S_{il(o)}^{aow}$  total liquid saturation when  $S_o^{aow}$  is varied at a constant  $S_w^{aow}$  (cm<sup>3</sup>/cm<sup>3</sup>).

- $S_{rl(w)}^{aow}$  total liquid saturation when  $S_w^{aow}$  is varied at a constant  $S_o^{aow}$  ( $\text{cm}^3/\text{cm}^3$ ).
- $\bar{S}$  effective saturation, equal to  $(S - S_{rw})/(1 - S_{rw} - S_{rN})$ .
- $w$  water.
- $W$  wetting fluid.
- $\alpha$  parameter (entry pressure) in van Genuchten  $P_c$ - $S$  model ( $\text{cm}^{-1}$ ).
- $\rho_b$  bulk density ( $\text{g}/\text{cm}^3$ ).
- $\rho_o$  density of oil ( $\text{g}/\text{cm}^3$ ).
- $\Sigma_{ij}$  coefficient for spreading of fluid  $i$  on fluid  $j$  (N/m).
- $\Sigma_{ij}^*$  contaminated coefficient for spreading (uses  $\sigma_{aw}^*$ ) of fluid  $i$  on fluid  $j$  (N/m).
- $\sigma_{aw}^*$  contaminated air-water interfacial tension (N/m).
- $\sigma_{ij}$  interfacial tension at interface between fluids  $i$  and  $j$  (N/m).
- $\phi_{sij}$  equilibrium contact angle at contact line between solid and fluids  $i$  and  $j$  (degrees).
- $\phi_{sij}^A$  advancing contact angle (degrees).
- $\phi_{sij}^R$  receding contact angle (degrees).
- $\lambda$  parameter (for shifting) the modified van Genuchten  $P_c$ - $S$  model (cm water).

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