E16

TRUE THREE-PHASE CAPILLARY ENTRY PRESSURES IN PORE-SCALE MODELLING

M.I.J. van Dijke and K.S. Sorbie

Department of Petroleum Engineering, Heriot-Watt University

Riccarton, Edinburgh EH14 4AS, UK

e-mail: rink@pet.hw.ac.uk

Introduction

In pore-scale modelling of three-phase flow it is commonly assumed that three-phase displacements can always be described as combinations of two-phase displacements. More specifically, the capillary entry pressures for piston-like displacements in three-phase flow are assumed to be the same as those in two-phase flow (e.g. [2,6,7,11]), hence calculation of two-phase capillary entry pressures would be sufficient. For two-phase flow the original method for derivation of capillary entry pressures in pores of non-circular has been developed by Mayer and Stowe [5] and Princen [8], the MS-P method. This powerful method equates the virtual work carried out by the main meniscus between the two phases and the change of surface free energy related to the corner fluid-fluid menisci and fluid-solid contacts. The approach has later been applied to various pore cross-sectional geometries, non-zero contact angles and contact angle hysteresis within a single pore (see [13] for references). For three-phase flow the fluid configurations have been calculated for various geometries, mainly for the sake of determining volumes and effective conductances (e.g. [14]), depending on the actual pressure differences, hence radii of curvatures of the fluid-fluid menisci. These configurations may be complicated by the presence of a layer of the intermediate-wetting phase [1].

Figure 1 – a. Configuration when gas displaces oil piston-like in a pore of triangular cross-section with water wetting films in the corners, b. cross-section of such a pore with bulk non-wetting gas phase and intermediate-wetting layer of oil.

In this work we challenge the assumption that three-phase displacements can always be described as combinations of two-phase displacements, supported by observations in the micromodel experiments carried out by [10]. In these experiments, displacements between two bulk phases take place in the presence of a corner film of the third phase, which can have different thicknesses i.e. different pressures. For example, in Figure 1a we show a pore of triangular cross-section in which gas displaces oil, but in the presence of a corner wetting film of water, while the films around gas and oil need not be of the same thickness. In Figure 1b a cross-section of such a pore is presented with the possible additional layer of oil separating gas and water. We extend the MS-P method to three-phase flow by calculating the capillary entry pressures for piston-like displacement of two phases in the presence of the remaining third phase. We allow arbitrary values of the contact angles, but assume that these are constant throughout the pore.

Derivation of capillary entry pressures

To determine the capillary entry pressures, we must analyse the possible phase occupancies of a single pore with polygonal cross-section, i.e. where individual corners as in Figure 1 can be distinguished, with corner half angle $\gamma \leq \pi/2$. At capillary equilibrium the pore cross-section may be occupied by one, two or all three phases, numbered as 1 non-wetting, 2 intermediate-wetting and 3 wetting. In a corner, the interfaces separating the various phases are denoted as arc menisci (AM). Assuming that AMs from different corners do not interfere, the occupancy of an entire pore cross-section is determined by the bulk phase occupancy and the occupancies of the individual corners. The actual existence of corner occupancies requires that the AMs geometrically fit in the corners, i.e. when the contact angles θ_{ij} , $ij = 12, 13, 23$ satisfy

$$\theta_{ij} \leq \pi/2 - \gamma \quad (1)$$

With bulk phase 1 and all three contact angles satisfying condition (1), an additional condition is needed for the presence of an intermediate-wetting layer as sketched in Figure 1b. A necessary purely geometrical condition for the existence of such a layer has been derived in [1,3].

Figure 2 – Examples of fluid configurations in the slice of a pore through two corners during displacement of phases 1 and 2, in b. the corners have different half angles.

For the piston-like displacement of one bulk phase by another, we must consider the possible pair of cross-sectional fluid configurations on either side of the main terminal meniscus (MTM) as shown in Figures 1a and 2. In Figure 2a, we find bulk phases 1 and 2 surrounded by films of different thicknesses. Obviously, if the various corners of a particular cross-section are different, the pairs of configurations may be different in each corner, as illustrated in Figure 2b, where additionally a layer of phase 2 separates phases 1 and 3 in the top corner. Furthermore, the corner at the bottom is too large to contain an AM between phases 1 and 3, hence the wetting film is absent.

The effective radius of curvature r_{ij} of a meniscus is determined by the difference $P_{ij} = P_i - P_j$ between the pressures of phases i and j on either side of the meniscus through the Laplace equation

$$P_{ij} = \sigma_{ij} / r_{ij} \quad (2)$$

where σ_{ij} denotes the interfacial tension. Obviously, far away from the MTM an AM is only curved in the cross-sectional plane of the pore as sketched in Figure 1a, therefore the corresponding r_{ij} is the radius of curvature in this plane. Throughout the pore the effective radii of the same interface type are identical, in particular of the MTM, despite its possibly complex geometry.

To derive the effective radii associated with the capillary entry pressures, we equate the virtual work W and the change of surface free energy ΔF [9], when moving the MTMs by a small distance dx in the direction along the pore. Our analysis employs the same technique as that of [5,8] but for three phases. If the pore cross-sections on either side of the MTM are entirely occupied by bulk phases i and j respectively, the virtual work is simply given by $W = P_{ij} A dx$ where A denotes the cross-sectional area

of the entire pore. The change in surface free energy is given by $\Delta F = (\sigma_{is} - \sigma_{js}) L_s dx$ where L_s denotes the total length of the pore walls and σ_{is} and σ_{js} denote the respective surface tensions

Figure 3 –Area $A_{ij}^{(\alpha)}$ occupied by phase j in corner α in the presence of bulk phase i . The lengths of the surrounding fluid-solid and fluid-fluid contacts are $L_{s,ij}^{(\alpha)}$ and $L_{f,ij}^{(\alpha)}$, respectively.

If one corner (α) of the pore contains AMs on both sides of the MTM, both the virtual work and the surface free energy change are adjusted. First, we define the cross-sectional area $A_{ij}^{(\alpha)}$ and the lengths of the surrounding fluid-solid and fluid-fluid contacts $L_{s,ij}^{(\alpha)}$ and $L_{f,ij}^{(\alpha)}$, indicated in Figure 3. Taking the fluid configuration in one of the corners of Figure 2b as an example, the virtual work expression changes into

$$W = (P_{12}A - P_{12}A_{23}^{(\alpha)} + P_{13}(A_{23}^{(\alpha)} - A_{13}^{(\alpha)}))dx \quad (3)$$

as phase 1 does not displace phase 2 in the cross-sectional area $A_{23}^{(\alpha)}$, but phase 1 does displace phase 3 in the area $A_{23}^{(\alpha)} - A_{13}^{(\alpha)}$. Furthermore, the expression for the surface free energy change is adjusted to

$$\Delta F = ((\sigma_{1s} - \sigma_{2s})L_s - \sigma_{1s}L_{s,13}^{(\alpha)} + \sigma_{2s}L_{s,23}^{(\alpha)} - \sigma_{3s}(L_{s,23}^{(\alpha)} - L_{s,13}^{(\alpha)}) + \sigma_{13}L_{f,13}^{(\alpha)} - \sigma_{23}L_{f,23}^{(\alpha)})dx \quad (4)$$

Equation (4) follows by considering that the fluid-solid contacts for phases 1 and 2 do not change along $L_{s,13}^{(\alpha)}$ and $L_{s,23}^{(\alpha)}$ respectively, but the contact of phase 3 decreases along $L_{s,23}^{(\alpha)} - L_{s,13}^{(\alpha)}$. Furthermore, the energy increases with the fluid-fluid contacts of length $L_{f,13}^{(\alpha)}$ and decreases with $L_{f,23}^{(\alpha)}$.

Using the definition $P_{13} = P_{12} + P_{23}$ in expression (3) and Young's equation $\sigma_{ij} \cos \theta_{ij} = \sigma_{is} - \sigma_{js}$ for the various fluid pairs to reduce expression (4), the energy balance $W = \Delta F$ becomes

$$(P_{12}A - P_{13}A_{13}^{(\alpha)} + P_{23}A_{23}^{(\alpha)})dx = (\sigma_{12} \cos \theta_{12} L_s + \sigma_{13}(L_{f,13}^{(\alpha)} - \cos \theta_{13} L_{s,13}^{(\alpha)}) - \sigma_{23}(L_{f,23}^{(\alpha)} - \cos \theta_{23} L_{s,23}^{(\alpha)}))dx \quad (5)$$

According to equation (2) for the various pressure differences, we may write equation (5) as

$$\sigma_{12}g(r_{12}, \theta_{12}) - \sigma_{13}g^{(\alpha)}(r_{13}, \theta_{13}) + \sigma_{23}g^{(\alpha)}(r_{23}, \theta_{23}) = 0 \quad (6)$$

where g and $g^{(\alpha)}$ are purely geometrical functions, defined as

$$g(r, \theta) = A/r - \cos \theta \cdot L_s \quad (7a)$$

$$g^{(\alpha)}(r, \theta) = A^{(\alpha)}(r, \theta)/r + L_f^{(\alpha)}(r, \theta) - \cos \theta \cdot L_s^{(\alpha)}(r, \theta) \quad (7b)$$

with $A^{(\alpha)}(r_{ij}, \theta_{ij}) = A_{ij}^{(\alpha)}$, $L_s^{(\alpha)}(r_{ij}, \theta_{ij}) = L_{s,ij}^{(\alpha)}$ and $L_f^{(\alpha)}(r_{ij}, \theta_{ij}) = L_{f,ij}^{(\alpha)}$. Basic trigonometry yields expressions for this area and these lengths, while expression (7b) reduces to

$$g^{(\alpha)}(r, \theta) = -A^{(\alpha)}(r, \theta)/r \quad (8)$$

with $A^{(\alpha)} = r^2 \cdot (\theta + \gamma^{(\alpha)} - \pi/2 + \cos\theta (\cos\theta / \tan\gamma^{(\alpha)} - \sin\theta))$. Notice, that $g^{(\alpha)} = 0$ if the corresponding interface is absent in corner α .

In equation (6), the first term reflects the energy balance for the bulk phase displacement if no AMs are present. The second term reflects the energy balance related to the AM surrounding bulk phase 1 and the third term reflects the energy balance related to the AM surrounding bulk phase 2. Hence, equation (6) can easily be generalised for a piston-like displacement in a pore with n corners

$$\begin{aligned} \sigma_{ij} g(r_{ij}, \theta_{ij}) - \sum_{\alpha=1}^n \left(\left\{ \sigma_{12} g^{(\alpha)}(r_{12}, \theta_{12}) + \sigma_{13} g^{(\alpha)}(r_{13}, \theta_{13}) + \sigma_{23} g^{(\alpha)}(r_{23}, \theta_{23}) \right\}_{side\ i} + \right. \\ \left. - \left\{ \sigma_{12} g^{(\alpha)}(r_{12}, \theta_{12}) + \sigma_{13} g^{(\alpha)}(r_{13}, \theta_{13}) + \sigma_{23} g^{(\alpha)}(r_{23}, \theta_{23}) \right\}_{side\ j} \right) = 0 \end{aligned} \quad (9)$$

where sides i and j indicate the sides of the MTM where bulk phases i and j respectively are present.

For a given geometry and a set of σ_{ij} and θ_{ij} equation (9) yields a relation between the three radii of curvature r_{ij} , $ij=12,13,23$. Combination of equation (2) and the definition $P_{13} = P_{12} + P_{23}$ provides an additional relation between the three radii,

$$\frac{\sigma_{13}}{r_{13}} = \frac{\sigma_{12}}{r_{12}} + \frac{\sigma_{23}}{r_{23}} \quad (10)$$

which reduces equation (9) to a functional relation between at most two of the radii of curvature. From equation (2) follow the pressure differences between the bulk phases and one of the remaining pressure differences. The pressure difference between the bulk phases is then taken as the capillary entry pressure $P_{c,ij}$, which may vary with one of the remaining pressure differences.

Possible solutions of equations (9) and (10) are restricted by the physical constraints that the radii must be positive and should not exceed a maximum or snap-off radius $r_{ij}^{\max}$ beyond which the AMs of a given type coalesce. Under some circumstances an additional solution may exist for a configuration where a layer of intermediate-wetting phase 2 is present, as for example shown in Figure 2b. We comment on these situations for a specific cross-sectional geometry in the next section.

Figure 4 – Dimensions of isosceles triangle with $\gamma^{(2)} = \gamma^{(3)}$.

Results for pores of triangular cross-section

We apply the above theory to a pore, of which the cross-section is an isosceles triangle, as sketched in Figure 4. The area and perimeter for this triangle are $A = r_w r_d$ and $L_s = 2(d + r_d)$, whereas the geometrical functions are given by equation (8), with $\tan \gamma^{(1)} = r_d / r_w$ and $\tan \gamma^{(2)} = (d - r_d) / r_w$. The snap-off radius $r^{\max}$ is found as

$$r^{\max} = \begin{cases} \frac{d}{\{\cos \theta / \tan \gamma^{(1)} - \sin \theta\} + \{\cos \theta / \tan \gamma^{(2)} - \sin \theta\}} & \text{if } \gamma^{(1)} \leq \gamma^{(2)} \\ \frac{r_d}{\cos \theta / \tan \gamma^{(2)} - \sin \theta} & \text{if } \gamma^{(1)} > \gamma^{(2)} \end{cases} \quad (11)$$

where the second term in the denominator of first expression vanishes if $\theta > \frac{\pi}{2} - \gamma^{(2)}$, i.e. if the corresponding AM does not fit in this corner. Similarly, the remaining terms in the denominators of equation (11) may vanish, yielding an infinite snap-off radius.

Firstly, we consider piston-like displacement of phases 1 and 2, when both phases are surrounded by a wetting film of phase 3 in all three corners, as sketched for gas, oil and water in Figure 2a. Then, equation (9) yields $\sigma_{12} g(r_{12}, \theta_{12}) - \sum_{\alpha=1}^3 (\sigma_{13} g^{(\alpha)}(r_{13}, \theta_{13}) - \sigma_{23} g^{(\alpha)}(r_{23}, \theta_{23})) = 0$. This equation depends on all three radii of curvatures, but it can be rewritten in terms of r_{13} and r_{23} only, using equations (6), (7a) and (10), leading to

$$\sigma_{13} (g(r_{13}, \theta_{13}) - g^{(1)}(r_{13}, \theta_{13}) - 2g^{(2)}(r_{13}, \theta_{13})) = \sigma_{23} (g(r_{23}, \theta_{23}) - g^{(1)}(r_{23}, \theta_{23}) - 2g^{(2)}(r_{23}, \theta_{23})) \quad (12)$$

Both sides of equation (12) lead to quadratic expressions in r_{13} and r_{23} respectively, hence the equation gives us a lengthy but explicit expression for one of these radii as a function of the other remaining radius. As mentioned above, if one of the contact angles does not satisfy equation (1) in a particular corner, the corresponding term $g^{(\alpha)}$ vanishes from equation (12), which then leads to a similar or even simpler solution. Anyway, combining equation (10) with the functional relation between r_{13} and r_{23} provides the radius r_{12} , which we take as the effective radius of the MTM for piston-like displacement. It may be clear that the corresponding capillary entry pressure $P_{c,12}$ varies with the pressure in the wetting film given by, say, P_{23} .

Secondly, if layers of phase 2 separate phases 1 and 3 as sketched in Figure 1b, equation (9) reduces to

$$\sigma_{12} (g(r_{12}, \theta_{12}) - g^{(1)}(r_{12}, \theta_{12}) - 2g^{(2)}(r_{12}, \theta_{12})) = 0 \quad (13)$$

which leads to a quadratic solution in terms of r_{12} . This solution would also be found in the two-phase situation where only phases 1 and 2 are present, for which expressions are given in [4]. It may be clear that the corresponding capillary entry pressure $P_{c,12}$ does not depend on the pressure in phase 3.

Thirdly, a more complicated equation arises when bulk phase 1 is surrounded by a layer of phase 2 in one of the corners and is directly surrounded by the wetting phase 3 in another corner. This situation can arise in case of unequal corners, where equation (1) is satisfied for θ_{12} in the first corner but not in the other. The resulting equation cannot be solved explicitly and this case is dealt with elsewhere [13].

We have calculated the solutions of equations (12) and (13) for a number of typical examples, where we take the three phases as 1=gas, 2=oil and 3=water, reflecting the wetting order in a water-wet pore. The shape of the triangle is varied through the aspect ratio $a = r_w/r_d$ (see Figure 4), the wettability of the pore is varied through the oil-water contact angle θ_{ow} and the oil spreading coefficient $C_{S,o} = \sigma_{gw} - \sigma_{go} - \sigma_{ow}$ is varied by changing the gas-oil interfacial tension σ_{go} . In fact, for the latter we only vary the ratio σ_{go}/σ_{ow} , whereas the value of the remaining ratio σ_{gw}/σ_{ow} is fixed at 1.2. The values of the remaining contact angles follow from the linear relations [12]

$$\begin{aligned} \cos\theta_{go} &= \{C_{S,o} \cos\theta_{ow} + C_{S,o} + 2\sigma_{go}\} / 2\sigma_{go} \\ \cos\theta_{gw} &= \{(C_{S,o} + 2\sigma_{ow})\cos\theta_{ow} + C_{S,o} + 2\sigma_{go}\} / 2\sigma_{gw} \end{aligned} \quad (14)$$

Furthermore, we use the dimensionless radii $\rho = r/r_{in}$, where $r_{in} = r_d(d - r_d)/r_w$ is the inscribed circle of the triangle. Results are presented as ρ_{go} , corresponding to the capillary entry pressure for gas-oil displacement, as a function of ρ_{ow} , representing the pressure in the wetting phase 3. The latter is normalised by the dimensionless snap-off radius $\rho_{ow}^{\max}$, which follows from equations (11). We consider only radii $\rho_{ow} < \rho_{ow}^{\max}$ as beyond this radius the pressures are such that snap-off of water by oil takes places before the gas-oil displacement can actually occur.

Figure 5 – Normalised radii of curvature for piston-like displacement of oil and gas in a pore of equilateral triangular cross-section for different values of σ_{go} , thus varying the oil spreading coefficient. For $\sigma_{go}/\sigma_{ow} = 0.2$ (spreading) and $\sigma_{go}/\sigma_{ow} = 0.4$ also constant solutions are shown, which correspond to displacement in the presence of oil layers around gas.

The effect of the spreading coefficient is presented in Figure 5 for a weakly water-wet pore, $\theta_{ow} = 1.0$ (radians) with equilateral triangular cross-section, $a = r_w/r_d = \sqrt{3}$. For a spreading oil, $\sigma_{go}/\sigma_{ow} = 0.2$, some variation of ρ_{go} occurs in the solution of equation (12). More importantly, as all three contact angles satisfy condition (1), oil layers may be present between water and gas, leading to an additional constant solution for ρ_{go} , which follows from equation (13). The deviation between the varying and the constant solution is small, but increases when considering a non-spreading oil with $\sigma_{go}/\sigma_{ow} = 0.4$. It is not clear, which of the two radii actually occurs, but at least the range of radii for which the layer solution exist is limited by a geometrical condition [1,3,13]. Notice that the varying solution changes from lying entirely below, to entirely above the constant solution. For $\sigma_{go}/\sigma_{ow} = 0.6$ condition (1) prevents occurrence of gas-oil interfaces and a constant solution corresponding to a situation with oil layers does

not exist. Furthermore, the variation of ρ_{go} increases when the spreading coefficient becomes more negative.

In Figure 6 results are presented for varying degree of wettability θ_{ow} and aspect ratio $a = r_w/r_d$ of the pore, while the interfacial tension ratio is now fixed as $\sigma_{go}/\sigma_{ow} = 0.4$. For $\theta_{ow} = 0$ (strongly water-wet) and $\theta_{ow} = 0.5$ both the gas-water and the oil-water interfaces fit in all three corners according to condition (1), as presented in Figure 6a. However, for $\theta_{ow} = 1.0$ the oil-water AM does no longer fit in the larger corners as $\pi/2 - \gamma^{(2)} = 0.955$. For $\theta_{ow} = 1.5$ none of the gas-water and oil-water AMs fit in any of the corners, hence all $g^{(\alpha)}$ in equation (22) vanish, leaving a simple equation for ρ_{go} with the presented constant solution. However, in this case gas-oil AMs do fit in all corners and gas is probably surrounded by an oil layer, but without water in the corner. This would lead to a different constant solution, following from equation (13). Notice that the variation of ρ_{go} decreases with increasing θ_{ow} , as the AMs disappear from the corners.

Also for different aspect ratios a the dependence of ρ_{go} on ρ_{ow} may be strong, as shown in Figure 6b, as well as non-monotonic. Additionally, the dependence on the aspect ratio is non-monotonic, which in itself is not so surprising as for both a smaller and larger than $\sqrt{3}$ (the equilateral triangle) the difference between the various corners grows. However, the equilateral triangle does not represent a limiting case, probably because of the asymmetry with respect to the size of the corners in triangles that result for a smaller and larger than $\sqrt{3}$ respectively. In both cases, there will be at least one relatively small corner that can contain all possible AMs.

Conclusions

We have derived a general formula for determination of the capillary entry pressures for piston-like displacement of two bulk phases in a pore with constant angular cross-section where also a third phase may be present. Conclusions are as follows:

- (i) The capillary entry pressures depend on the pressure in the remaining third phase, if present, and is from different any two-phase capillary entry pressure. The only exception arises when the non-wetting phase is completely separated from the wetting phase by layers of the intermediate-wetting phase. If a capillary entry pressure depends on the pressure of the third phase, we refer to it as “varying”, otherwise it is called “constant”.
- (ii) For the presented capillary entry pressures two restrictions on the occurrence of the corresponding piston-like displacements apply: (a) if the radius of curvature associated with one of the AMs, that is assumed present, becomes too large, piston-like displacement is prevented by snap-off of one of the bulk phases; (b) layers of phase 2 can only be present for a limited range of radii of curvatures.
- (iii) For pores of triangular cross-section effects on the gas-oil capillary entry pressures of the oil spreading coefficient, the degree of wettability and the pore aspect ratio have been investigated. In most cases strong and non-monotonic dependence of the effective gas-oil radius of curvature on the oil-water radius is found. Constant solutions have been taken into account for the equilateral triangle, where they occur for spreading and near-spreading conditions only.

Acknowledgement

The authors would like to thank the following members of the Heriot-Watt WAG Consortium for supporting this research: The UK Department of Trade and Industry, BP, Shell, PDVSA, BHP, TotalFinaElf, Norsk Hydro and Statoil.

Figure 6 –Normalised radii of curvature for piston-like displacement of oil and gas in a pore of equilateral triangular cross-section for a. varying degree of wettability θ_{ow} (with $a = 2.83$ fixed) and b. varying aspect ratio a (with $\theta_{ow} = 1.0$ fixed).

References

- [1] Fenwick, D.H. and Blunt, M.J.: 1995, "Pore Level Modelling of Three Phase Flow in Porous Media", Proceedings of the 8th European Symposium on Improved Oil Recovery, Vienna, Austria, May 1995.
- [2] Fenwick, D.H. and Blunt, M.J.: 1998, "Three-Dimensional Modeling of Three Phase Imbibition and Drainage, *Advances in Water Resources*, **21**, 121-143.
- [3] Firincioglu, T, Blunt, M.J. and Zhou, D.: 1999, "Three-Phase Flow and Wettability Effects in Triangular Capillaries", *Colloids and Surfaces, A. Physicochemical and Engineering Aspects*, **155**, 259-276.
- [4] Ma, S., Mason, G. and Morrow, N.R.: 1996, "Effect of Contact Angle on Drainage and Imbibition in Regular Polygonal Tubes", *Colloids and Surfaces, A. Physicochemical and Engineering Aspects*, **117**, 273-291.
- [5] Mayer, R.P. and Stowe, R.A.: 1965, "Mercury Porosimetry – Breakthrough Pressure for Penetration between Packed Spheres", *J. Colloid Interface Sci.*, **20**, 893-911.
- [6] Øren, P.E. and Pinczewski, W.V.: 1995, "Fluid Distributions and Pore-Scale Displacement Mechanisms in Drainage Dominated Three-Phase Flow", *Transport in Porous Media* **20**, 105-133.
- [7] Pereira, G.G., Pinczewski, W.V., Chan, D.Y.C., Paterson, L. and Øren, P.E.: 1996, "Pore-Scale Network Model for Drainage-Dominated Three-Phase Flow in Porous Media", *Transport in Porous Media*, **24**, 167-201.
- [8] Princen, H.M.: 1969, "Capillary Phenomena in Assemblies of Parallel Cylinders. I. Capillary Rise between Two Cylinders", *J. Colloid Interface Sci.*, **30**, 69-75.
- [9] Rowlinson, J.S. and Widom, B.: 1989, *Molecular Theory of Capillarity*, Clarendon Press, Oxford.
- [10] Sohrabi, M., Henderson, G., Tehrani, D.H. and Danesh A.: 2000, "Visualisation of Oil Recovery by Water Alternating Gas (WAG) Injection - Water Wet System", SPE63000, Proceedings of the SPE Annual Technical Conference and Exhibition, Dallas, TX, October 2000.
- [11] Soll, W.E. and Celia, M.A.: 1993, "A Modified Percolation Approach to Simulating Three-Fluid Capillary Pressure-Saturation Relationships", *Adv. Water Resour.*, **16**, 107-126.
- [12] van Dijke, M.I.J., Sorbie K.S. and McDougall, S.R.: 2001 "Saturation-Dependencies of Three-Phase Relative Permeabilities in Mixed-wet and Fractionally-Wet Systems", *Advances in Water Resources* **24**, 365-384.
- [13] van Dijke, M.I.J. and Sorbie K.S.: 2002 "Three-phase capillary entry conditions in pores of non-circular cross-section", Submitted to *J. Colloid Interface Sci.*
- [14] Zhou, D., Blunt, M. and Orr, F.M.: 1997, "Hydrocarbon Drainage along Corners of Noncircular Capillaries", *J. Colloid Interface Sci.*, **187**, 11-21.