

Relationship Between Zeta Potential and Wettability in Porous Media: Insights From a Simple Bundle of Capillary Tubes Model.

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1. Introduction

Wetting describes the tendency of one fluid to spread over a solid surface in the presence of a second fluid. Wettability defines the degree of wetting. In many subsurface settings, including hydrocarbon reservoirs [1-3], CO₂ storage reservoirs [4-11] and contaminated aquifers [12, 13], wettability is a key property, because it controls the pore-scale distribution of fluids and therefore the dynamics of multiphase flow [13-17].

The wettability of crude-oil-brine-rock (COBR) systems has recently received increased attention because of the abundant evidence that wettability alteration occurs during improved oil recovery (IOR) in response to controlled salinity waterflooding (CSW) [18-20]. Evidence from core-flooding experiments has indicated that IOR is associated with a change in wettability to a more water-wet state, while experiments on model systems have shown decreased contact angle/area, and reduced adhesion of real or model crude oils, in response to changing brine composition [21-28].

Experimental studies have also demonstrated a link between the wettability of intact core samples and macro-scale zeta potential of the samples, measured using the streaming potential method (SPM) [18, 29, 30]. The macro-scale zeta potential measured in porous media or powder suspensions represents a complex average over the micro (mineral-surface)-scale zeta potentials, that may vary across different minerals in heterogeneous (multi-mineral) samples, or across the different faces of a given mineral in homogenous (single mineral) samples [31]. Such macro-scale zeta potential measurements, obtained using the SPM on porous media or the electrophoretic method (EPM) on powder suspensions, are very common [18, 29, 30, 32-38] (see [39] for a review).

Jackson and co-workers [18, 29, 30] found that the measured macro-scale zeta potential measured in intact carbonate rock samples changed after the wettability of the samples was modified by

aging in crude oil. The wettability of the samples after aging was characterised using the Amott-Harvey water wetting index [40] defined as

$$I_W = \frac{V_{WSI}}{V_{WSI} + V_{WFI}} \quad (1)$$

where V_{WSI} is the volume of water spontaneously imbibed into the sample at the irreducible water saturation, and $V_{WSI} + V_{WFI}$ is the total volume of water than can be injected into the sample [41]. Aging is an experimental protocol that facilitates the wettability-altering reactions thought to occur in reservoirs after they are charged with oil: an initially water-saturated rock sample is drained with the crude oil of interest, and then stored at elevated temperature for several weeks (e.g. [30]).

The measured change in macro-scale zeta potential with wettability reported by Jackson and co-workers [18, 29, 30] followed two broad trends. In one group of carbonate samples, the measured zeta potential became more negative as the samples became more oil-wet; in the other group, the zeta potential became more positive (Figure 1). The groups were not separated by rock type: samples of a given rock type plotted in either group. Rather, the groups were separated by crude oil type: four of the tested crude oils consistently showed more negative zeta potential after aging, while the other three consistently showed more positive zeta potential.

Jackson and co-workers interpreted the observed trends using a simple, qualitative, pore-scale model. They argued that mineral surfaces (or parts thereof) that become oil-wet return the micro-scale zeta potential of the oil-brine interface, rather than the mineral-brine interface (Figure 1). Moreover, samples which are measured to be less water-wet using the Amott-Harvey index have a greater proportion of oil-wet mineral surfaces. The macro-scale zeta potential measured in oil-wet samples is dominated by the micro-scale zeta potential of the oil-brine interface, rather than the mineral-brine interface. Thus, if the measured zeta potential becomes more negative as the samples become increasingly oil-wet, then the oil-brine interface has a zeta potential that is more negative than the mineral-brine interface (Figure 1). Conversely, if the measured zeta potential becomes more positive as the samples become increasingly oil-wet, then the oil-brine interface has a zeta potential that is more positive than the mineral-brine interface (Figure 1). If the measured zeta potential remains unchanged, then the mineral-brine and oil-brine zeta potentials are the same.

Although this simple model can explain, conceptually, the observed experimental behaviour, it does not provide a quantitative relationship between macro-scale zeta potential and wettability in

1 porous media. Such a relationship requires a pore-scale model, the development of which is the
2 main aim of this paper. A pore-scale model can also yield new insight into the relationship between
3 macro-scale zeta potential and water saturation, for which there are almost no experimental data
4 [18, 29]. The lack of experimental data relating macro-scale zeta potential and water saturation in
5 porous media provides further motivation for the development of a pore-scale model.

6
7 Given that this is the first model of its type, we consider the simplest possible description of the
8 rock pore-space that captures the necessary physics: a bundle of capillary tubes of different size.
9 Although it is a much-simplified representation of the pore-space of a reservoir rock, the model is
10 useful because it allows the governing equations to be derived from first principles (see [42] for
11 examples in single phase flow). A capillary tubes model is the simplest possible approach to relate
12 micro-scale (mineral-surface-scale) and macro-scale (continuum-scale) properties of wettability
13 and zeta potential; such models have been extensively used to investigate and quantify streaming
14 potentials during single and multi-phase flow in water-wet systems [43-52]. Understanding the
15 behaviour of such simple models underpins the development and application of pore-scale models
16 that capture more realistic representations of pore geometry, fluid occupancy and connectivity
17 [53].

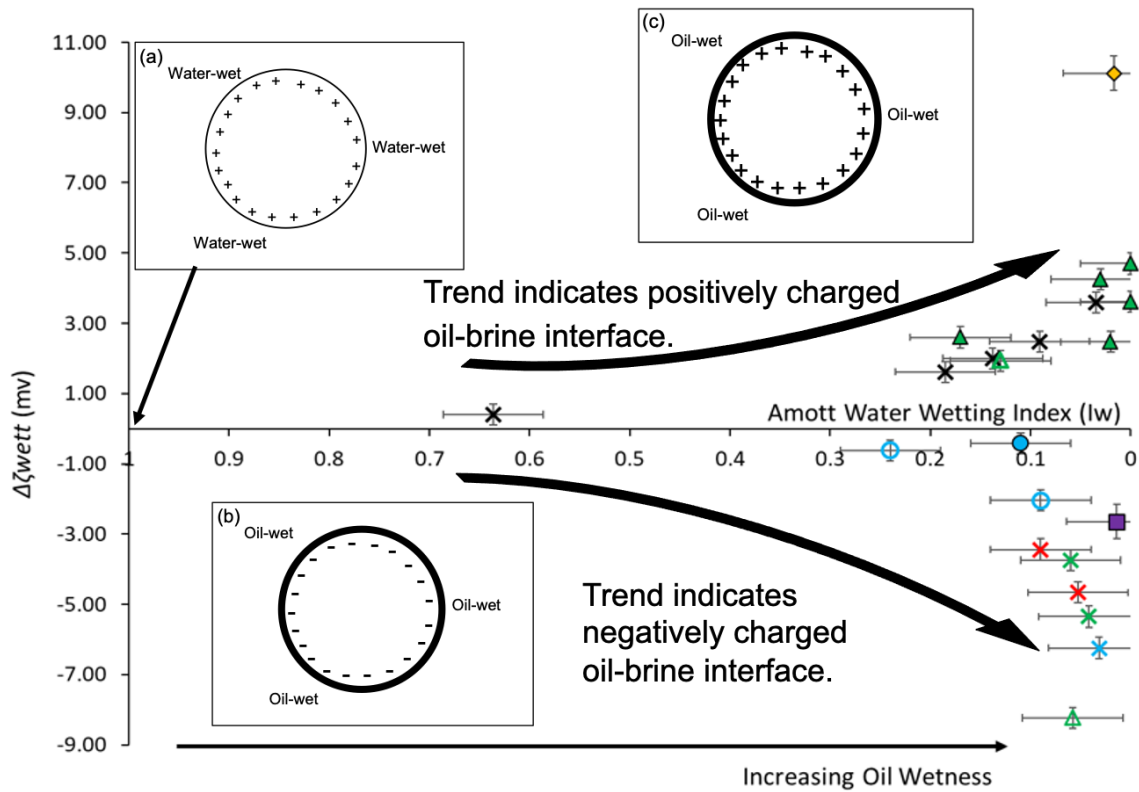


Figure 1 – Experimental data (adapted from [29]) showing the change in macro-scale zeta potential measured on intact natural carbonate cores after drainage and aging with crude oil and natural saline brine. Triangles represent measurements made at room temperature and circles represent measurements made at elevated temperature ($>70^{\circ}\text{C}$). The different colours represent different crude oils (see [29] for more details). Data plotted as a function of the Amott-Harvey water wetting index (I_w). Inset (a) is a schematic of a model capillary that is water-wet and brine saturated. The mineral surface of the capillary has a positive micro-scale zeta potential in this example, consistent with the experimental data reported in [29] for the carbonate cores investigated. Inset (b) represents samples in which the measured macro-scale zeta potential becomes more negative after wettability alteration. The micro-scale oil-brine zeta potential is negative, so the macro-scale zeta potential becomes more negative as more of the mineral surfaces become oil-wet. Inset (c) represents samples in which the measured macro-scale zeta potential becomes more positive after wettability alteration. The micro-scale oil-brine zeta potential is positive and larger in magnitude than the mineral-brine zeta potential, so the macro-scale zeta potential becomes more positive as more of the mineral surfaces become oil-wet.

2. Bundle of Capillary Tubes Model

The bundle of capillary tubes model used in this paper is derived from similar models used in previous studies [49, 54, 55]. The macro-scale properties of interest here are water saturation, Amott-Harvey water-wetting index (equation 1), and zeta potential. To determine these properties, we need to calculate total and water-saturated pore (capillary) volumes, and the electrokinetic coupling in water-saturated capillaries. We outline the key equations and derivations from first principles. The model derivation first considers a single capillary tube with radius r_c , occupied by a single phase; we then integrate over all capillaries with different phase occupancy and values of r_c to determine the macro-scale properties for the entire model. We extend the capillary tubes model beyond previous studies by assigning a different micro-scale zeta potential to water- and oil-wet capillaries, and calculating the resulting macro-scale wettability index and zeta potential to provide the first quantitative relationship between wettability and zeta potential for a simple model of a porous medium.

2.1. Volume and Electrokinetic Coupling in a Single Capillary

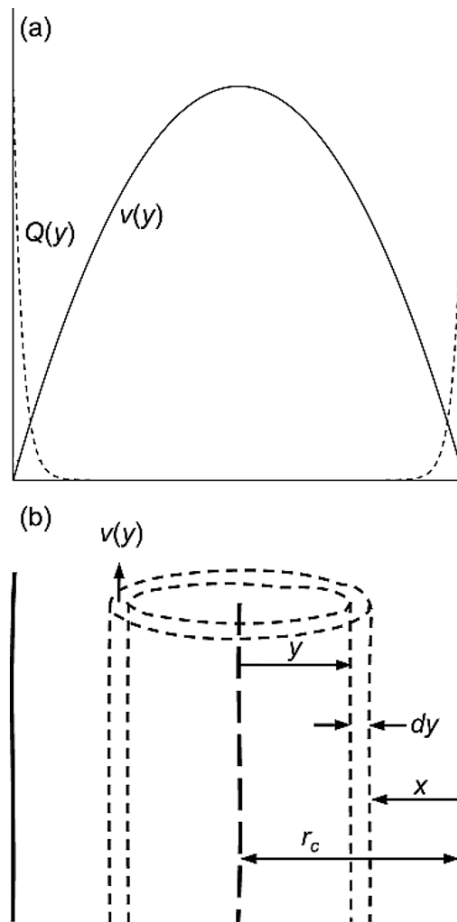


Figure 2: (a) Flow velocity $v(y)$ (solid line) and excess countercharge $Q(y)$ (dashed line) within a brine-occupied capillary, invoking the thin double-layer assumption and a constant surface charge density. The width of the thin double layer has been greatly exaggerated. (b) Calculation of the streaming current. Modified from [54].

We begin by considering a single, water-occupied capillary of length L and radius r_c . The volume of the capillary is trivially given by

$$V_c = \pi r_c^2 L \quad (2)$$

We assume that only water (brine) and oil are present in the model, denoted by the subscripts w and o respectively. Each capillary is occupied by a single, mobile, fluid phase, but the capillaries can be wetted by a thin layer of either phase. This wetting layer is immobile and volumetrically insignificant relative to the total volume of the capillary, and thus does not contribute to the phase saturation. The capillary tube is assumed to be initially water-wet and can become oil-wet only if it has been invaded by oil.

The streaming potential within the capillary arises from the electrical charge on the capillary surface. In this model, we consider the capillaries to be comprised of homogenous calcium carbonate and assume a constant surface charge density. Calcium carbonate was chosen to be consistent with the experimental data against which the model predictions are compared [18, 29, 36]. Although it is immobile and volumetrically insignificant, the wetting layer is important because it dictates the surface charge. Water-wet, brine-occupied capillaries exhibit the charge at the carbonate-brine interface. Conversely, oil-wet, brine-occupied capillaries exhibit the charge at the oil-brine interface: polar species present in the oil can modify the surface charge during wettability alteration (Figure 2; see also Figure 1 in [29]).

The charge on the capillary surface results in the development of an electrical double layer (EDL). We assume the EDL comprises a layer of fixed, immobile ions (the ‘Stern layer’ [42]), separated at the Stern plane from a ‘diffuse layer’ of mobile ions. To describe the excess charge in the diffuse layer, $Q(y)$, we invoke the “thin double layer assumption” which is valid when the thickness of the electrical double layer is much smaller than the local radius of curvature. This assumption has been shown to be valid in reservoir rocks [56].

During brine flow, relative motion of the excess charge in the diffuse layer along the shear plane yields a streaming current. The location of the shear plane is a variable often tuned to match experimental zeta potential data [57]. Here we employ the simplest assumption that the shear plane coincides with the Stern plane and thus define the effective radius of each capillary to be the distance from the Stern plane to the centre line of the capillary (Figure 2). Oil is assumed to be

non-conductive and to carry no electrical charge, consistent with experimental data [1] consequently, the flow of oil through oil occupied capillaries does not generate a streaming current and is not considered here.

Applying boundary conditions of steady laminar flow of brine into and out of the capillary, the streaming current through a single capillary is given by [42]:

$$I_{s,c} = \int_0^{r_c} 2\pi y Q(y) v(y) dy \quad (3)$$

The velocity profile, $v(y)$, across the capillary is described by Poiseuille's law (Figure 2a):

$$v(y) = \frac{1}{4\mu} (r_c^2 - y^2) \frac{\Delta P}{L} \quad (4)$$

where μ is the viscosity of the brine, y is the distance from the centre of the capillary (Figure 2b) and ΔP is the pressure drop along the capillary of length L .

The double layer is confined to a thin region near the wall of the capillary and, following [42] and numerous other textbooks, we use this to linearize Poiseuille's equation close to the capillary wall to give

$$(r_c^2 - y^2) \approx 2r(r - y) \quad (5)$$

Substituting $x = (r - y)$, equation (3) becomes

$$I_{s,c} = \int_0^{r_c} \frac{2\pi(r-x)rx\Delta P}{2\mu L} Q(x) dx \quad (6)$$

We use the thin nature of the double layer further to linearize the streaming current, giving

$$r^2 \left(x - \frac{x^2}{r} \right) \approx r^2 x \quad (7)$$

The charge density in the EDL $Q(x)$ can be described by Poisson's equation [42]:

$$\varepsilon \frac{d^2 V}{dx^2} = Q(x) \quad (8)$$

where ε is the permittivity of the brine which we assume constant and V is the electrical potential in the diffuse layer. Substituting equations (7) and (8) into equation (6) and integrating by parts yields an expression for the streaming current through a single capillary, in terms of the zeta potential of the capillary surface, the brine viscosity and permittivity, and the pressure gradient along the capillary.

In water-wet capillaries, the micro-scale zeta potential of the capillary surface corresponds to the carbonate mineral-brine interface (ζ_{mb}) whereas in oil-wet capillaries, the micro-scale zeta potential of the capillary surface corresponds to the oil-brine interface (ζ_{ob}). The streaming current in each case is given, respectively, by

$$I_{S,C} = \frac{-\varepsilon \zeta_{mb} \pi r_c^2 \Delta P}{\mu L} \quad (9a)$$

$$I_{S,C} = \frac{-\varepsilon \zeta_{ob} \pi r_c^2 \Delta P}{\mu L} \quad (9b)$$

We now apply boundary conditions of zero current flow into or out of the capillary and no charge accumulation at the end of the capillary [42]. The streaming current must then be balanced by a conduction current of equal magnitude but opposite direction. The conduction current in a single capillary is given by Ohm's law [42]:

$$I_{C,C} = \pi r_c^2 \sigma_b \frac{\Delta V}{L} + 2\pi r_c \sigma_s \frac{\Delta V}{L} \quad (10)$$

where ΔV is the streaming potential difference across the capillary, σ_b is the conductivity of the brine and σ_s is the surface conductivity due to the presence of the EDL. Oil-occupied capillaries are non-conductive.

Equating the streaming and conduction currents, consistent with the boundary conditions, and rearranging yields:

$$\frac{\Delta V}{\Delta P} = C = \frac{\varepsilon \zeta_{mb}}{\mu(\sigma_b + \frac{2\sigma_s}{r})} \quad (11a)$$

$$\frac{\Delta V}{\Delta P} = C = \frac{\varepsilon \zeta_{ob}}{\mu(\sigma_b + \frac{2\sigma_s}{r})} \quad (11b)$$

for water-wet, brine-occupied, and oil-wet, brine-occupied capillaries respectively, where C is termed the streaming potential coupling coefficient. If we neglect surface electrical conductivity, as is typical in highly conductive, saline brines, these equations simplify to the well-known Helmholtz-Smoluchowski equation:

$$\frac{\Delta V}{\Delta P} = C = \frac{\varepsilon \zeta_{mb}}{\mu \sigma_b} \quad (12a)$$

$$\frac{\Delta V}{\Delta P} = C = \frac{\varepsilon \zeta_{ob}}{\mu \sigma_b} \quad (12b)$$

for water-wet and oil-wet capillaries, respectively. If surface electrical conductivity is negligible, the relationship between the coupling coefficient and zeta potential is independent of the capillary tube properties i.e. the model microstructure [42]:

2.2. Bundle of Capillary Tubes

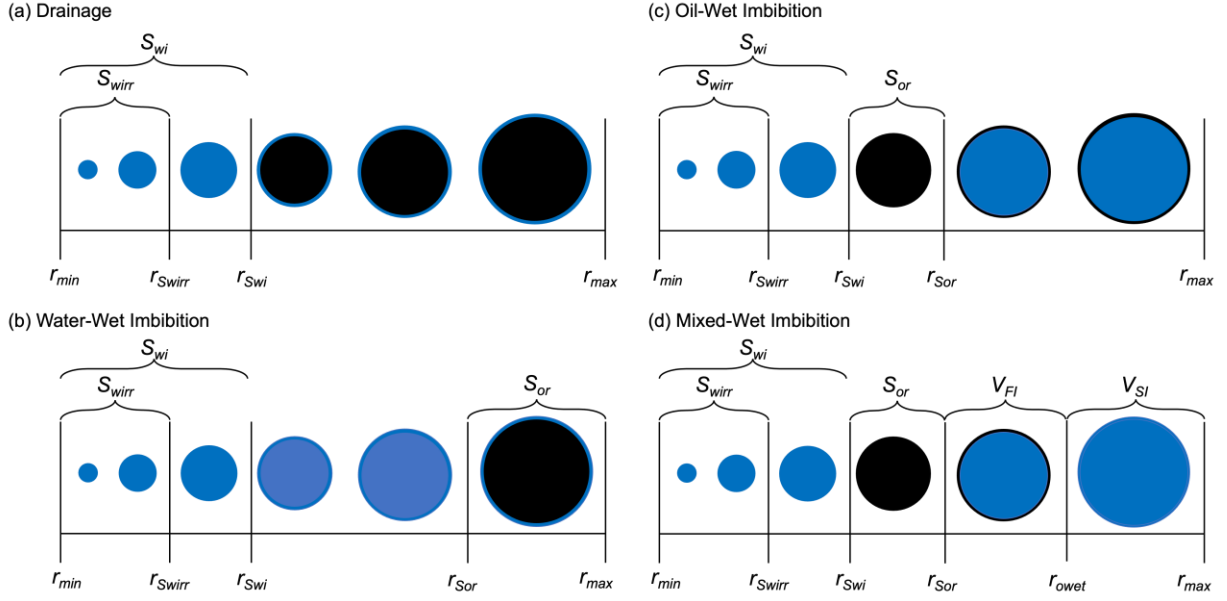


Figure 3 - Schematic of the bundle of capillary tubes model for (a) drainage and (b-d) imbibition with different wetting states. (b) shows the case where all capillaries remain water-wet after drainage and aging; (c) shows the case where oil-invaded capillaries become oil-wet after drainage and aging, and (d) shows the case where only the smaller pores become oil-wet after drainage and aging to yield a mixed-wet model.

We now extend the single capillary model to a bundle containing N capillaries orientated in the same direction, with no intersections between capillaries, which results in unidirectional mass and charge transport. The capillaries have different radii to allow for varying fluid occupancy. The number of capillaries with radius between r_i and $r_i + dr_i$ is given by $n(r_i)dr_i$ such that integrating over all capillaries gives:

$$\int_{r_{min}}^{r_{max}} n(r_c) dr_c = N \quad (13)$$

where r_{min} and r_{max} are the minimum and maximum capillary radii respectively. In this paper we consider 1000 capillaries, the radii of which are determined by a simple capillary size distribution of the form:

$$n(r)dr_c = D \left(\frac{r - r_{max}}{r_{min} - r_{max}} \right)^c \quad (14)$$

where c takes integer values between 0 and 12 [54] and D is a constant dependent on the values of N and c . Larger values of c skew the distribution to increase the frequency of smaller pores which is observed in many geological porous media [16]. This simple expression allows us to

quantitatively investigate the effect of the pore-size distribution on the model zeta potential and wettability.

The mobile phase occupying each capillary is determined assuming capillary equilibrium. There is no need to specify or calculate a capillary number, but we assume it to be sufficiently large enough for capillary equilibrium. During drainage, when the (initially) non-wetting oil phase invades the (initially) water-wet capillaries, the oil invades the capillaries in order of size, from largest to smallest [58] (Figure 3a). During imbibition (defined here as invasion of water into the capillaries resulting in an increase in the water saturation), the water invades water-wet capillaries first in the order smallest to largest (Figure 3a), before invading oil-wet capillaries in the order largest to smallest (Figure 3b).

The general procedure for calculating the macro-scale bulk and transport properties of the model (described in [55]) is simple: the property is defined for a single capillary as shown in the preceding section, and then the macro-scale value is determined by integrating over all capillaries that contribute.

The water saturation is given by the volume of water-occupied capillaries divided by the total capillary (pore) volume, noting that water may occupy the largest or smallest capillaries depending on the wettability. We define r_{omin} to be the radius of the smallest water-wet capillary that is occupied by oil and vary this to vary the water saturation in water-wet models. Similarly, we define r_{omax} to be the radius of the largest oil-wet capillary that is occupied by oil, and vary this to vary the water saturation in oil-wet models. In mixed-wet models we vary both r_{omin} and r_{omax} to vary the water saturation in water- and oil-wet portions of the model, as described in a later section. Given this, the water saturation is generally expressed as:

$$S_w = \frac{\int_{r_{min}}^{r_{omin}} r_c^2 n(r_c) dr_c + \int_{r_{omax}}^{r_{max}} r_c^2 n(r_c) dr_c}{\int_{r_{min}}^{r_{max}} r_c^2 n(r_c) dr_c} \quad (15)$$

with the expression for a given wetting state obtained by adjusting the values of r_{omin} and r_{omax} . These values are discussed for specific wetting scenarios in later sections.

The macro-scale properties of Amott-Harvey water-wetting index and zeta potential are calculated in similar fashion and we explain these in the following section. Before doing so, we address the

modelling of initial, irreducible and residual water and/or oil saturation. Expressions for other macro-scale model properties such as porosity and permeability can be found in [54] but are not relevant here.

2.3. Initial, Irreducible & Residual Saturations

Without suitable modification, the bundle of capillary tubes does not allow for the trapping of phases observed in natural porous media: drainage continues until all the capillaries are occupied by the invading oil phase and $S_w = 0$; likewise, imbibition continues until all the capillaries are occupied by the invading water phase and $S_w = 1$. In real porous media, water is trapped in the smaller pores and the corners of larger pores during drainage. The minimum water saturation, typically termed the irreducible water saturation, S_{wirr} , is therefore some value greater than zero. In some cases, during drainage, the invading oil does not displace all the mobile water, resulting in some initial water saturation $S_{wi} > S_{wirr}$.

2.3.1. Irreducible Water Saturation

To account for the irreducible water saturation, we simply define a minimum radius, r_{Swirr} , which can be invaded by oil during drainage (Figure 3a); capillaries with smaller radii than this minimum value represent the small pores in rocks that are not invaded during primary drainage, yielding an irreducible water saturation given by:

$$S_{wirr} = \frac{\int_{r_{min}}^{r_{Swirr}} r_c^2 n(r_c) dr_c}{\int_{r_{min}}^{r_{max}} r_c^2 n(r_c) dr_c} \quad (16)$$

Capillaries with $r_c < r_{Swirr}$ remain water-wet and water-occupied and this water is trapped and immobile: it contributes to the electrical conductivity of the model but not to the streaming current. We can adjust the value of r_{Swirr} to match experimental data for S_{wirr} .

2.3.2. Initial Water Saturation

To account for an initial water saturation $S_{wi} > S_{wirr}$, we define a minimum radius of capillaries r_{Swi} which are invaded by oil during drainage; capillaries with smaller radii than this minimum value represents the smaller pores in rocks that are nonetheless larger than those occupied by irreducible water and could be invaded during primary drainage, yielding an initial water saturation given by:

$$S_{wi} = \frac{\int_{r_{min}}^{r_{Swi}} r_c^2 n(r_c) dr_c}{\int_{r_{min}}^{r_{max}} r_c^2 n(r_c) dr_c} \quad (17)$$

Capillaries with $r_{Swir} < r_c < r_{omin}$ remain water-wet and water-occupied but the water is mobile and contributes to the electrical conductivity and streaming current. If oil displaces water from all mobile capillaries, $r_{Swi} = r_{Swir}$ and equation (17) reduces to equation (16). We can adjust the value of r_{Swi} to match experimental data for S_{wi} .

2.3.3. Residual Oil Saturation

During imbibition, residual oil is trapped either by snap-off when the oil ganglia in water-wet pores become disconnected, or when flow through wetting layers in oil-wet pores becomes too slow [53]. The water saturation during imbibition returns to some maximum value given by $S_w = 1 - S_{or}$, where S_{or} is the residual oil saturation. The capillary tubes model cannot capture the details of snap-off and layer flow. Instead, the approach used to account for the residual oil saturation depends on the wetting state of the model.

In a water-wet model, we define a maximum radius of oil-occupied capillaries r_{Sor} that can be invaded by water during imbibition (Figure 3b), assuming that capillary forces cause the wetting water to initially invade the smaller capillaries leaving oil trapped in the larger capillaries. Conversely, in an oil-wet model, we define a minimum radius of oil-occupied capillaries r_{Sor} that can be invaded by water during imbibition (Figure 3c), assuming that capillary forces cause the non-wetting water to initially invade the larger capillaries, leaving oil trapped in the smaller capillaries. This approach yields a residual oil saturation given by:

$$S_{or} = \frac{\int_{r_{Sor}}^{r_{max}} r_c^2 n(r_c) dr_c}{\int_{r_{min}}^{r_{max}} r_c^2 n(r_c) dr_c} \quad (\text{water-wet}) \quad (18a)$$

$$S_{or} = \frac{\int_{r_{Swir}}^{r_{Sor}} r_c^2 n(r_c) dr_c}{\int_{r_{min}}^{r_{max}} r_c^2 n(r_c) dr_c} \quad (\text{oil-wet, } S_{wi} = S_{wir}) \quad (18b)$$

$$S_{or} = \frac{\int_{r_{Swi}}^{r_{Sor}} r_c^2 n(r_c) dr_c}{\int_{r_{min}}^{r_{max}} r_c^2 n(r_c) dr_c} \quad (\text{oil-wet, } S_{wi} > S_{wir}) \quad (18c)$$

Capillaries containing immobile residual oil do not contribute to either the electrical conductivity or streaming current. We can adjust the value of r_{Sor} to match experimental data for S_{or} .

2.4. Macro-Scale (Model) Zeta Potential and Amott-Harvey Water Wetting Index

The streaming current is determined by integrating over all capillaries that are occupied by mobile brine ($r_c > r_{Swirr}$), since we assume oil to be non-conductive. Water-wet capillaries contribute to the streaming current that arises from the surface charge at the mineral-brine interface; oil-wet capillaries contribute to the streaming current that arises from the surface charge at the oil-brine interface. The total streaming current for the model is the sum of these two contributions, since only water or oil can wet the capillary surface.

Consistent with the boundary conditions defined for a single capillary and assuming the pressure drop across the model is constant, the total streaming current is balanced by the total conduction current. The conduction current is determined by integrating over all brine-occupied capillaries, irrespective of whether the brine is mobile ($r_c > r_{Swirr}$) or irreducible ($r_c < r_{Swirr}$). The exact expressions depend on the model wetting state, which is discussed next.

As we show later, the model predictions are independent of the absolute size of the capillaries and the size distribution. This is because we assume surface electrical conductivity is negligible for the saline brines of interest, so the streaming and conduction currents follow the same paths through the pore-space and so scale in the same way [49, 54, 59]. We assume here only that capillaries are similar in diameter to reservoir rock pores and so small enough to justify our assumption that phase occupancy is dictated by capillary equilibrium; we also assume that the model is large enough to correspond to a representative elementary volume (REV). Similar assumptions underpin more complex pore-scale models [53].

2.4.1. Drainage and Water-Wet Imbibition

We assume the model remains water-wet during drainage (Figure 3(a)). To calculate the macroscopic zeta potential of the entire model, we integrate equation (9a) over all mobile, brine-occupied capillaries to determine the streaming current of the model. We vary the value of r_{omin} to vary the water saturation such that $r_{Swirr} < r_c < r_{omin}$. The streaming current of the model as a function of water saturation is given by:

$$I_{S,M}(S_w) = \int_{r_{Swirr}}^{r_{omin}} \frac{-\epsilon \zeta_{mb} \pi r_c^2 \Delta P}{\mu L} d(r_c) \quad (19)$$

Likewise, the total conduction current of the model is calculated by integrating equation (10) over all brine-occupied capillaries, varying r_{omin} to vary the water saturation, yielding:

$$I_{C,M}(S_w) = \int_{r_{min}}^{r_{omin}} \pi r_c^2 \sigma_b \frac{\Delta V}{L} d(r_c) + \int_{r_{min}}^{r_{omin}} 2\pi r_c \sigma_s \frac{\Delta V}{L} d(r_c) \quad (20)$$

Equations (19) and (20) must balance to honour the boundary conditions of zero current flow and zero charge accumulation, but to enforce this we need to account for the irreducible water saturation. We scale (19) and (20) by the total volume of capillaries through which the streaming and conduction currents act at $S_w = 1$, such that the normalised streaming and conduction currents are, respectively, given by:

$$I_{S,Mn}(S_w) = \frac{\int_{r_{Swirr}}^{r_{omin}} \frac{-\varepsilon \zeta_{mb} \pi r_c^2 \Delta P}{\mu L} d(r_c)}{\int_{r_{min}}^{r_{max}} r_c^2 d(r_c)} \quad (21)$$

$$I_{C,Mn}(S_w) = \frac{\left(\int_{r_{min}}^{r_{omin}} \pi r_c^2 \sigma_b \frac{\Delta V}{L} d(r_c) + \int_{r_{min}}^{r_{omin}} 2\pi r_c \sigma_s \frac{\Delta V}{L} d(r_c) \right)}{\left(\int_{r_{min}}^{r_{max}} r_c^2 d(r_c) + \int_{r_{min}}^{r_{max}} r_c d(r_c) \right)} \quad (22)$$

Equating equations (21) and (22) and re-arranging yields the following expression for the macro-scale coupling coefficient:

$$\frac{\Delta V}{\Delta P} = C(S_w) = \frac{\varepsilon \zeta_{mb} \left(\frac{\int_{r_{Swirr}}^{r_{omin}} r_c^2 n(r_c) dr_c}{\int_{r_{Swirr}}^{r_{max}} r_c^2 n(r_c) dr_c} \right)}{\mu \left(\frac{\sigma_b \int_{r_{min}}^{r_{omin}} r_c^2 n(r_c) dr_c + \sigma_s \int_{r_{min}}^{r_{omin}} r_c}{\int_{r_{min}}^{r_{max}} r_c^2 n(r_c) dr_c + \int_{r_{min}}^{r_{max}} r_c} \right)} \quad (23)$$

Equation (23) is the Helmholtz-Smoluchowski equation for our water-wet bundle of capillaries model and accounts for the saturation dependence of the streaming potential coupling coefficient.

The corresponding water saturation is given by equation (15) with $r_{omax} = r_{max}$.

If we set $r_{omin} = r_{max}$, then $S_w = 1$ from equation (15), and equation (23) simplifies to equation (11a) for a single brine occupied, water-wet capillary. Given that we will compare model predictions against measured data obtained using saline brines, we ignore surface electrical conductivity and set $\sigma_s = 0$. Substituting for C in equation (23) and re-arranging gives the macro-scale zeta potential

of the water-wet model as a function of the micro-scale zeta potential of the mineral-brine interface (ζ_{mb}):

$$\zeta(S_w) = \frac{\zeta_{mb} \left(\frac{\int_{r_{Swirr}}^{r_{omin}} r_c^2 n(r_c) dr_c}{\int_{r_{min}}^{r_{max}} r_c^2 n(r_c) dr_c} \right)}{\left(\frac{\int_{r_{min}}^{r_{omin}} r_c^2 n(r_c) dr_c}{\int_{r_{min}}^{r_{max}} r_c^2 n(r_c) dr_c} \right)} \quad (24)$$

Equation (24) applies during both drainage and imbibition, so long as the capillaries are all water-wet. However, during imbibition, we can choose to limit the maximum value of r_{omin} to account for the residual oil saturation, such that $r_{omin} \leq r_{Sor}$ (Figure 3b). As before, the corresponding water saturation is given by equation (15) with $r_{omax} = r_{max}$.

At the irreducible water saturation, all water-wet capillaries occupied by mobile oil will spontaneously imbibe a volume of brine given by:

$$V_{WSI} = \int_{r_{Swirr}}^{r_{Sor}} \pi r_c^2 L n(r_c) dr_c \quad (25)$$

The total volume of capillaries that can be invaded by brine during spontaneous and forced imbibition is equivalent to the total volume of capillaries occupied by mobile oil (i.e. that do not contain immobile water or residual oil so have $r_{Swirr} < r_c < r_{Sor}$). The total volume of brine that can invade is therefore given by

$$V_{WSI} + V_{WFI} = \int_{r_{Swirr}}^{r_{Sor}} \pi r_c^2 L n(r_c) dr_c \quad (26)$$

Given this, and the definition in equation (1), the corresponding Amott water-wetting index for a water-wet model is given by

$$I_w = \frac{\int_{r_{Swirr}}^{r_{Sor}} r_c^2 n(r_c) dr_c}{\int_{r_{Swirr}}^{r_{Sor}} r_c^2 n(r_c) dr_c} \quad (27)$$

which trivially returns the value of 1 in the water-wet case.

2.4.2. Oil-Wet Imbibition

If the oil-occupied capillaries become oil-wet after drainage (i.e. the crude oil causes wettability alteration, Figure 3c) then the macro-scale zeta potential during imbibition is calculated using the same approach as outlined for the water-wet case: we integrate the streaming current over all capillaries occupied by mobile brine, and the conduction current over all brine-occupied capillaries. However, oil-wet capillaries now contribute to the streaming current that arises from the oil-brine zeta potential. If $r_{Swi} = r_{Swirr}$, then the initial water saturation equals the irreducible water saturation and only oil-wet capillaries contribute to the streaming current. However, if $r_{Swi} > r_{Swirr}$ then the initial water saturation is higher than the irreducible water saturation ($S_{wi} > S_{wirr}$), so the water-wet, brine-occupied capillaries (i.e. those with $r_{Swirr} < r_c < r_{Swi}$) also contribute to the streaming current that arises from the mineral-brine zeta potential. We vary r_{omax} to vary the water saturation, as the invading brine now invades oil-wet capillaries in the order largest to smallest. Following the same approach as outlined for the water-wet case, we obtain the following expressions for the macro-scale zeta potential as a function of the micro-scale zeta potentials of the mineral-brine (ζ_{mb}) and oil-brine (ζ_{ob}) interfaces

$$\zeta(S_w) = \frac{\zeta_{ob} \left(\frac{\int_{r_{omax}}^{r_{max}} r_c^2 n(r_c) dr_c}{\int_{r_{Swirr}}^{r_{max}} r_c^2 n(r_c) dr_c} \right)}{\left(\frac{\int_{r_{min}}^{r_{Swirr}} r_c^2 n(r_c) dr_c + \int_{r_{omax}}^{r_{max}} r_c^2 n(r_c) dr_c}{\int_{r_{min}}^{r_{max}} r_c^2 n(r_c) dr_c} \right)} \quad (S_{wi} = S_{wirr}) \quad (28a)$$

$$\zeta(S_w) = \frac{\zeta_{mb} \left(\frac{\int_{r_{Swirr}}^{r_{Swi}} r_c^2 n(r_c) dr_c}{\int_{r_{Swirr}}^{r_{max}} r_c^2 n(r_c) dr_c} \right) + \zeta_{ob} \left(\frac{\int_{r_{omax}}^{r_{max}} r_c^2 n(r_c) dr_c}{\int_{r_{Swirr}}^{r_{max}} r_c^2 n(r_c) dr_c} \right)}{\left(\frac{\int_{r_{min}}^{r_{Swi}} r_c^2 n(r_c) dr_c + \int_{r_{omax}}^{r_{max}} r_c^2 n(r_c) dr_c}{\int_{r_{min}}^{r_{max}} r_c^2 n(r_c) dr_c} \right)} \quad (S_{wi} > S_{wirr}) \quad (28b)$$

where we can choose to limit the minimum value of r_{omax} to account for the residual oil saturation such that $r_{omax} \geq r_{sor}$. The corresponding water saturation is given by equation (15), with $r_{omin} = r_{Swirr}$ if $S_{wi} = S_{wirr}$ and $r_{omin} = r_{Swi}$ if $S_{wi} > S_{wirr}$.

In this oil-wet model, irrespective of the value of S_{wi} , there are no oil-occupied, but water-wet capillaries that can spontaneously imbibe water, so the corresponding Amott water wetting index trivially returns the value of 0.

2.4.3. Mixed-Wet Imbibition

Mixed wettability in our model occurs when some of the oil-occupied capillaries do not undergo wettability alteration to become oil-wet after aging. Controls on wettability alteration for a given crude oil and formation brine are complex and include the mineral surface properties and the local topology of the pore-space [60-64]. Our simple model cannot account for these complexities, so we consider two ‘end-member’ cases of mixed wettability: (i) the smallest-oil occupied capillaries remain water-wet after aging and (ii) the largest oil-occupied capillaries remain water-wet after aging (e.g. Figure 3d). As we show in the results, the model predictions are identical irrespective of which of these two approaches we choose to handle mixed-wettability; the results for mixed-wetting are independent of the distribution of water- and oil-wet capillaries.

We define a new radius r_{owet} to account for mixed wettability. In mixed-wetting case (i), all capillaries with $r_{Swi} < r_c < r_{owet}$ remain water-wet after aging and all capillaries with $r_c > r_{owet}$ become oil-wet. Oil occupied, but water-wet, capillaries will spontaneously imbibe water whilst oil-wet capillaries occupied by mobile oil will imbibe additional water under an applied pressure. Following the same approach described in the previous sections, the Amott water-wetting index for case (i) is given by:

$$I_w = \frac{\int_{r_{Swi}}^{r_{owet}} r_c^2 n(r_c) dr_c}{\int_{r_{Swi}}^{r_{owet}} r_c^2 n(r_c) dr_c + \int_{r_{Sor}}^{r_{max}} r_c^2 n(r_c) dr_c} \quad (29)$$

We can adjust the value of r_{owet} to match experimental data for I_w .

Water-wet capillaries return the zeta potential of the mineral-brine interface whilst oil-wet capillaries return the zeta potential of the oil-brine interface so. We vary the water saturation by varying r_{omin} in water-wet capillaries such that $r_{omin} \leq r_{owet}$ and vary r_{omax} in oil-wet capillaries such that $r_{omax} \geq r_{Sor}$ noting that the invading water will occupy water-wet capillaries first at capillary equilibrium. We can adjust the value of r_{Sor} to match experimental data for S_{or} . The macro-scale zeta potential is given by

$$\zeta(S_w) = \frac{\zeta_{mb} \left(\frac{\int_{r_{Swirr}}^{r_{omin}} r_c^2 n(r_c) dr_c}{\int_{r_{Swirr}}^{r_{max}} r_c^2 n(r_c) dr_c} \right) + \zeta_{ob} \left(\frac{\int_{r_{Sor}}^{r_{omax}} r_c^2 n(r_c) dr_c}{\int_{r_{Swirr}}^{r_{max}} r_c^2 n(r_c) dr_c} \right)}{\left(\frac{\int_{r_{min}}^{r_{omin}} r_c^2 n(r_c) dr_c + \int_{r_{Sor}}^{r_{omax}} r_c^2 n(r_c) dr_c}{\int_{r_{min}}^{r_{max}} r_c^2 n(r_c) dr_c} \right)} \quad (30)$$

The corresponding water saturation is given by equation (15).

If $r_{owet} = r_{Sor}$ then equation (30) reduces to equation (24) and we recover the water-wet imbibition model ($I_w = 1$). If $r_{owet} = r_{Swirr}$ then equation (30) reduces to equation (28a) while if $r_{owet} = r_{Swi}$ then equation (29) reduces to equation (28b); in both cases, we recover the oil-wet imbibition model ($I_w = 0$).

For mixed-wetting case (ii), all capillaries with $r_{Swi} < r_c < r_{owet}$ become oil-wet after aging and all capillaries with $r_c > r_{owet}$ remain water-wet. The Amott water wetting index in this case is given by:

$$I_w = \frac{\int_{r_{owet}}^{r_{max}} r_c^2 n(r_c) dr_c}{\int_{r_{owet}}^{r_{max}} r_c^2 n(r_c) dr_c + \int_{r_{Sor}}^{r_{owet}} r_c^2 n(r_c) dr_c} \quad (31)$$

and the macro-scale zeta potential by:

$$\zeta(S_w) = \frac{\zeta_{mb} \left(\frac{\int_{r_{owet}}^{r_{max}} r_c^2 n(r_c) dr_c}{\int_{r_{Swirr}}^{r_{max}} r_c^2 n(r_c) dr_c} \right) + \zeta_{ob} \left(\frac{\int_{r_{Sor}}^{r_{owet}} r_c^2 n(r_c) dr_c}{\int_{r_{Swirr}}^{r_{max}} r_c^2 n(r_c) dr_c} \right)}{\left(\frac{\int_{r_{owet}}^{r_{max}} r_c^2 n(r_c) dr_c + \int_{r_{Sor}}^{r_{owet}} r_c^2 n(r_c) dr_c}{\int_{r_{min}}^{r_{max}} r_c^2 n(r_c) dr_c} \right)} \quad (S_{wi} = S_{wirr}) \quad (32a)$$

$$\zeta(S_w) = \frac{\zeta_{mb} \left(\frac{\int_{r_{Swirr}}^{r_{Swi}} r_c^2 n(r_c) dr_c}{\int_{r_{Swirr}}^{r_{max}} r_c^2 n(r_c) dr_c} \right) + \zeta_{mb} \left(\frac{\int_{r_{owet}}^{r_{max}} r_c^2 n(r_c) dr_c}{\int_{r_{Swirr}}^{r_{max}} r_c^2 n(r_c) dr_c} \right) + \zeta_{ob} \left(\frac{\int_{r_{Sor}}^{r_{owet}} r_c^2 n(r_c) dr_c}{\int_{r_{Swirr}}^{r_{max}} r_c^2 n(r_c) dr_c} \right)}{\left(\frac{\int_{r_{min}}^{r_{Swi}} r_c^2 n(r_c) dr_c + \int_{r_{owet}}^{r_{max}} r_c^2 n(r_c) dr_c + \int_{r_{Sor}}^{r_{owet}} r_c^2 n(r_c) dr_c}{\int_{r_{min}}^{r_{max}} r_c^2 n(r_c) dr_c} \right)} \quad (S_{wi} > S_{wirr}) \quad (32b)$$

The corresponding water saturation is given by equation (15).

If $r_{owet} = r_{Swi}$ then equations (32a) and (32b) reduce to equation (24) and we recover the water-wet imbibition model ($I_w = 1$); if $r_{owet} = r_{max}$ then equations (32a) and (32b) reduce to equations (28a) and (28b) respectively, and we recover the oil-wet imbibition model ($I_w = 0$).

3. Results

3.1. Water-Wet and Oil-Wet Models Drained to S_{wirr}

We begin by considering the case when rock samples are drained to the irreducible water saturation, S_{wirr} , with crude oil before aging at elevated temperature to induce wettability alteration. This procedure is common to many petrophysical laboratories and studies [18, 65, 66]. We model this by assuming all capillaries are initially water-wet and water occupied and are then invaded by crude oil until all of the mobile capillaries are occupied by oil, yielding $r_{omin} = r_{Swirr}$ and $r_{omax} = r_{max}$ (Figure 3a). We first investigate the zeta potential measured during the subsequent imbibition process in the simplest, limiting scenarios in which none, or all, of the oil-invaded capillaries undergo wettability alteration, yielding completely water- or oil-wet models with $I_w = 1$ or 0 respectively.

For our example results, we use a value of $\zeta_{mb} = +7\text{mV}$ for the micro-scale zeta potential of the mineral-brine interface, as reported for carbonate samples saturated with a saline natural brine (>2 Mol/L) [18] and consistent with other measurements of carbonate rocks saturated with typical saline natural brines [29, 32, 67]. We explore a range of values for the micro-scale zeta potential of the oil-brine interface, ζ_{ob} , as its magnitude and polarity are both uncertain at the conditions of interest here. We discuss this issue later in the paper. We report the macro-scale zeta potential as a function of water saturation, with the imbibition curves returning to a water saturation of 1. In natural rock samples, this would not occur due to trapping of residual oil, but the curve can simply be terminated at the chosen residual oil saturation ($S_w = 1 - S_{or}$) to interpret results for a specific example.

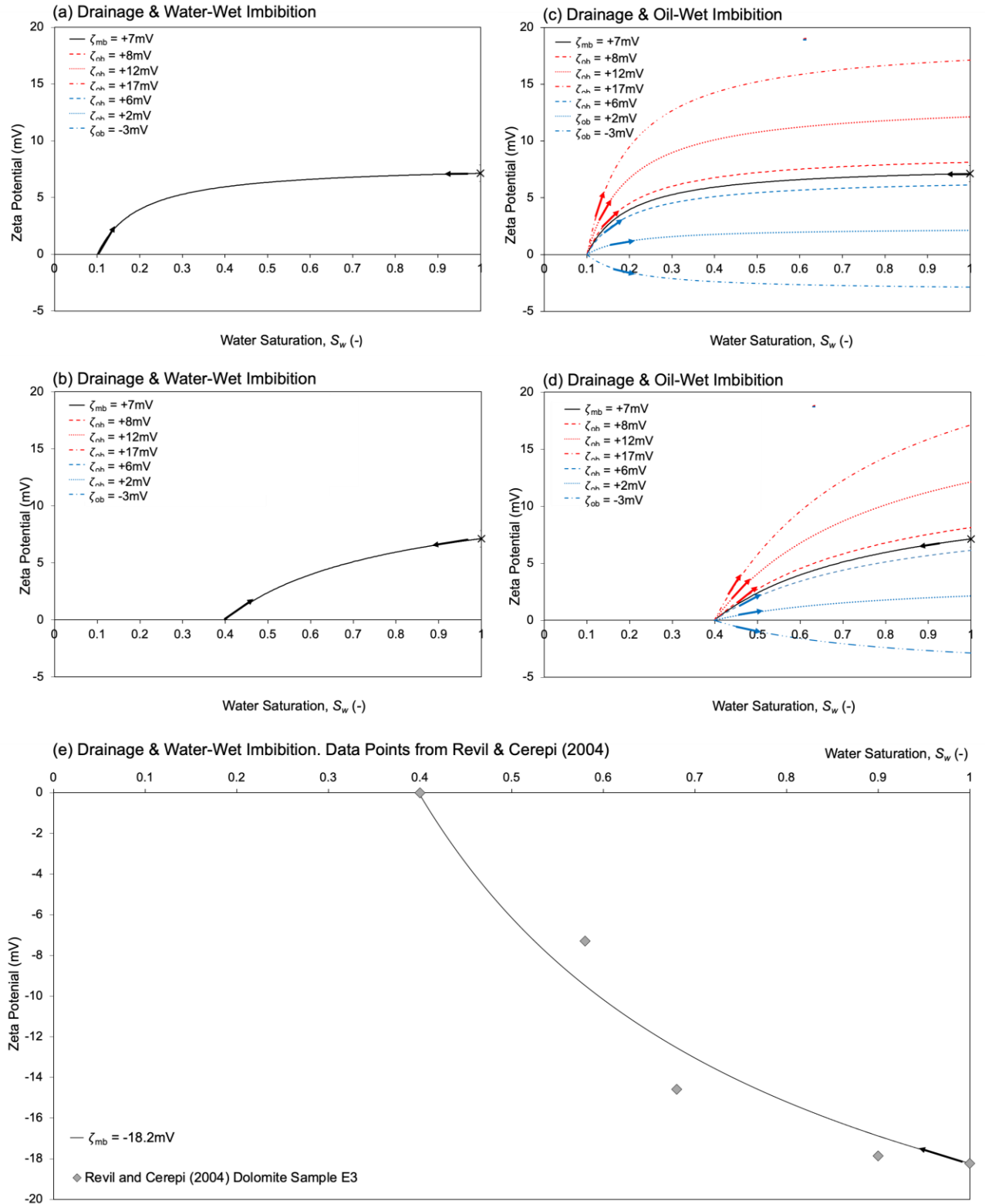


Figure 4 – Macro-scale (model) zeta potential as a function of water saturation for an example with micro-scale mineral-brine zeta potential $\zeta_{mb} = +7\text{ mV}$ for (a) drainage and water-wet imbibition with $S_{wirr} = 0.1$; (b) drainage and water-wet imbibition with $S_{wirr} = 0.4$; (c) drainage and oil-wet imbibition with $S_{wirr} = 0.1$; (d) drainage and oil-wet imbibition with $S_{wirr} = 0.4$ and a range of values of oil-brine zeta potential. Plot (e) shows drainage with $S_{wirr} = 0.4$, compared against experimental data obtained from Revil and Cerepi (2004) [36] and using their measured value of $\zeta_{mb} = -18.2\text{ mV}$ in our model. Measured zeta potential values were calculated from their reported streaming potential measurements using the Helmholtz-Smoluchowski equation (12a), assuming negligible surface electrical conductivity consistent with their measured conductivity data and using published correlations for brine viscosity and permittivity

[68]. Arrows show direction of water saturation change. Red curves represent models where $\zeta_{ob} > \zeta_{mb}$; blue curves represent models where $\zeta_{ob} < \zeta_{mb}$.

The macro-scale (model) zeta potential obtained during water-wet drainage and both water- and oil-wet imbibition monotonically decreases with decreasing water saturation and falls to zero at the irreducible water saturation (Figure 4). The capillary size distribution has no effect on the macro-scale zeta potential irrespective of wetting state or water saturation i.e. the model microstructure has no impact on the results when bulk electrical conductivity dominates, consistent with numerous previous experimental and modelling studies [42, 49, 59]. The reason the microstructure plays no role is that the streaming and conduction currents follow the same paths through the pore-space [49, 59]. Our focus here on saline brines with high electrical conductivity means that surface electrical conductivity is small compared to the bulk electrical conductivity, as has been observed in numerous studies [29,30,32,36,37].

We compare our model predictions against measured macro-scale zeta potential values obtained from steady-state, gas-brine streaming potential measurements on a water-wet dolomite rock sample reported by Revil and Cerepi (2004) (their sample E3) [36]. They measured the streaming potential coupling coefficient at full and partial saturation during drainage using 5 g/L (0.086M) NaCl electrolyte and nitrogen.

Our model predictions were obtained by setting $S_{irr} = 0.4$ and using a micro-scale mineral-brine zeta potential of $\zeta_{mb} = -18.2\text{mV}$, consistent with the experimentally determined values. There are no other adjustable parameters in the model. The model predictions and experimental data show good agreement for this water-wet sample, despite the simplicity of the model. Note that Revil and Cerepi (2004) did not report error bars. There are no comparable data for oil-wet samples against which we can test the model predictions.

Figure 4 shows that the modelled and measured macro-scale zeta potentials decrease in magnitude with decreasing water saturation. This is because the streaming and conduction currents both decrease as the water saturation decreases, but the streaming current decreases more rapidly than the conduction current as the irreducible (immobile) water contributes to the latter but not the former. At the irreducible saturation, there is no flow of water, so the streaming current and hence the sample zeta potential fall to zero [54]. Varying the value of S_{irr} acts only to stretch or compress the curves (Figure 4) consistent with previous findings [49]. When the irreducible water saturation

1 is large, the macro-scale zeta potential decreases in magnitude more rapidly with decreasing water
2 saturation and *vice-versa*. In the limiting case of zero irreducible water saturation, the macro-scale
3 zeta potential is constant and independent of water saturation as both the streaming and
4 conduction currents decrease at the same rate [54].

5
6 The saturation dependence of the model macro-scale zeta potential during water-wet drainage and
7 imbibition is identical irrespective of the chosen micro-scale oil-brine zeta potential (Figure 4a,b,e).
8 In both processes, all capillaries are water-wet and so the streaming current is controlled only by
9 the zeta potential at the mineral-brine interface.

10
11 In contrast, the saturation dependence of the model macro-scale zeta potential during (water-wet)
12 drainage and oil-wet imbibition can be strongly hysteretic depending on the difference between
13 the micro-scale oil-brine and mineral-brine zeta potentials (Figure 4c,d). If the oil-brine zeta
14 potential is more positive than the mineral-brine zeta potential, then the macro-scale zeta potential
15 becomes relatively more positive with increasing water saturation; conversely, if the oil-brine zeta
16 potential is less positive or negative, then the macro-scale zeta potential becomes relatively less
17 positive with increasing water saturation and may even invert to return a negative value. The reason
18 is that the oil-occupied capillaries all become oil-wet after drainage, so the streaming current during
19 imbibition is controlled only by the micro-scale zeta potential at the oil-brine interface. The results
20 suggest that, if the residual oil saturation was very small, it would be possible to determine the zeta
21 potential of the oil-brine interface by measuring the streaming potential on a strongly oil-wet
22 porous sample. However, rock samples aged in natural crude oils rarely show purely water- or oil-
23 wet conditions, so we need to investigate the effect of mixed wettability on the model zeta
24 potential.

25 26 3.2. Mixed-Wet Models

27 We test here the effect of having an initial water saturation that is larger than the irreducible
28 saturation. Having determined that model results are not significantly affected by its value, we set
29 $S_{wirr} = 0.3$ as a representative average and use the same micro-scale mineral-brine zeta potential of
30 $\zeta_{mb} = +7$ mV as in the previous section. As before, we report the saturation dependence of the
31 macro-scale zeta potential with the imbibition curves returning to a water saturation of 1, but the
32 curve can simply be terminated at the chosen residual oil saturation ($S_w = 1 - S_{or}$) to interpret results
33 for a specific example.

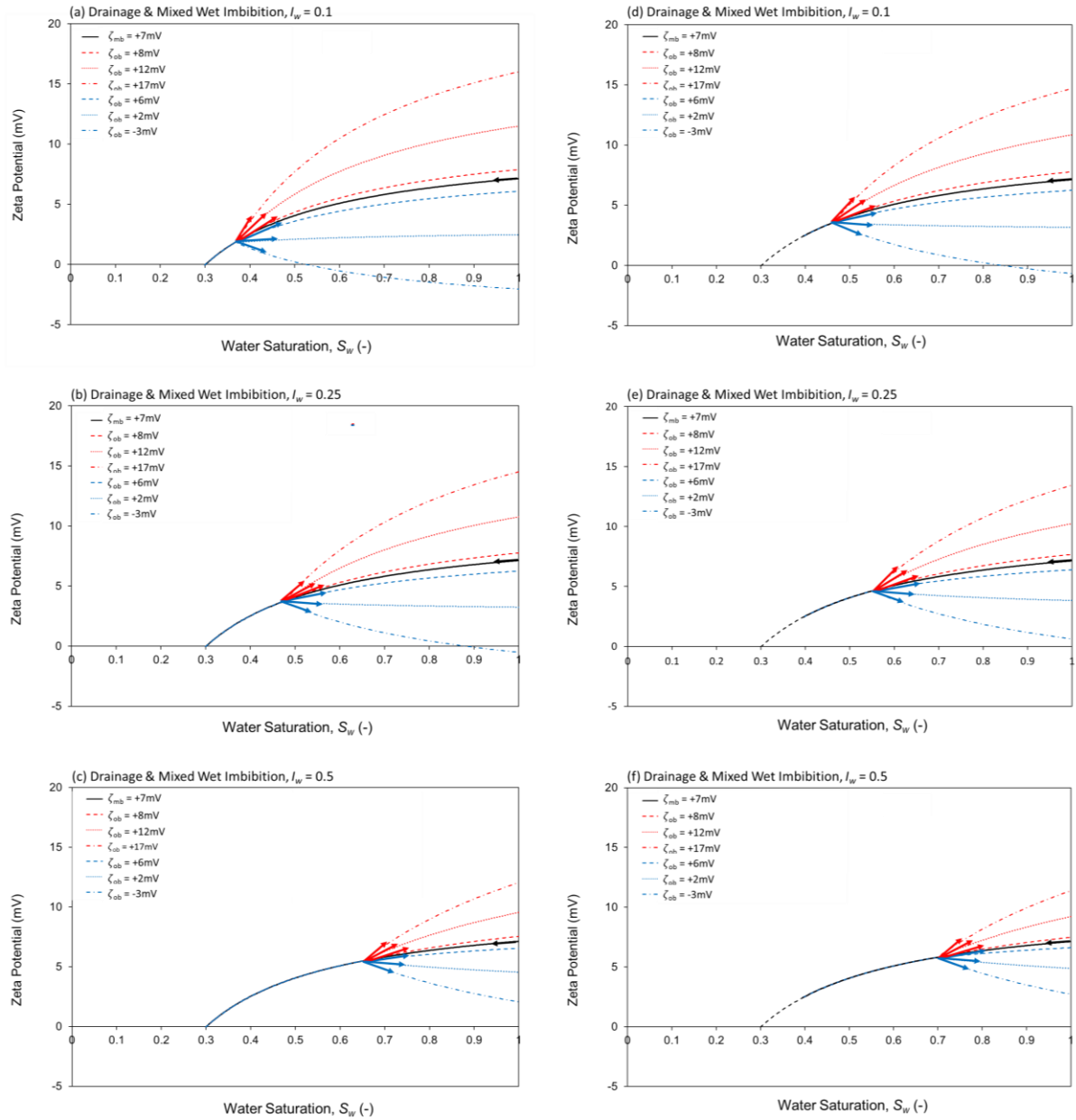


Figure 5 – Macro-scale (model) zeta potential as a function of water saturation for (a-c) (water-wet) drainage and mixed-wet imbibition for samples drained to $S_{wirr} = 0.3$ with $I_w = 0.1, 0.25$ and 0.5 respectively and for (d-f) (water-wet) drainage and mixed-wet imbibition for samples drained to $S_{wirr} = 0.4$ with $S_{wirr} = 0.3$ and $I_w = 0.1, 0.25$ and 0.5 respectively. The dashed portion of the drainage curve shows the path that would be followed if drainage were to continue to S_{wirr} . Arrows show direction of water saturation change. Red curves represent models where the micro-scale $\zeta_{ob} > \zeta_{mb}$; blue curves represent models where $\zeta_{ob} < \zeta_{mb}$.

As before, the capillary size distribution has no effect on the saturation dependence of the macro-scale zeta potential; we also find that results are identical irrespective of the approach used to model mixed-wetting (cases (i) and (ii) described above). The model microstructure, including the wettability-dependent distribution of oil and brine, once again plays no role, for the same reason given in the previous section: the streaming and conduction currents follow the same paths

1 through the rock pore space. Microstructure only impacts the predicted macro-scale zeta potential
2 if the streaming and conduction currents follow different paths.

3
4 In contrast to the end-member water- and oil-wet cases investigated in the previous section, we
5 now observe hysteresis between (water-wet) drainage and mixed-wet imbibition (Figure 5). The
6 macro-scale zeta potential during drainage is again controlled only by the micro-scale zeta potential
7 at the mineral-brine interface; however, during imbibition, the macro-scale zeta potential arises
8 from a combination of the micro-scale mineral-brine zeta potential in the water-wet capillaries and
9 oil-brine zeta potential in the oil-wet capillaries.

10
11 The imbibition curves initially follow the drainage curve because the invading water displaces oil
12 from water-wet capillaries first, so only the micro-scale mineral-brine zeta potential contributes to
13 the streaming current. Once the water-wet capillaries are all occupied, the imbibition curves
14 diverge from the drainage curve because the invading water enters oil-wet capillaries, so the micro-
15 scale oil-brine zeta potential also contributes to the streaming current. As before, if the oil-brine
16 zeta potential is more positive than the mineral-brine zeta potential, then the macro-scale zeta
17 potential becomes relatively more positive with increasing water saturation; conversely, if the oil-
18 brine zeta potential is less positive or negative, then the macro-scale zeta potential becomes
19 relatively less positive with increasing water saturation.

20
21 The results more closely reflect water-wet imbibition with increasing I_w and/or S_{wi} because fewer
22 capillaries become oil-wet after drainage (Figure 5). A negative micro-scale zeta potential at the
23 oil-brine interface is not always sufficient to invert the polarity of the macro-scale zeta potential.
24 There must be enough capillaries that become oil-wet and/or the micro-scale oil-brine zeta
25 potential must be sufficiently large and different to the mineral-brine zeta potential to have a
26 significant impact on the macro-scale zeta potential. These results suggest that the macro-scale
27 zeta potential measured on a mixed-wet sample is unlikely to reflect the magnitude of the micro-
28 scale oil-brine zeta potential and may not reflect its polarity even when measured at the residual
29 oil saturation, when water occupies many of the oil-wet pores. We further test the relationship
30 between wettability and the macro-scale zeta potential measured at the residual saturation in the
31 next section.

3.3. Interpretation of the Micro-Scale Zeta Potential of the Oil-Brine Interface

Thus far we have used the capillary tubes model to predict general trends between macro-scale zeta potential, wetting state and the micro-scale zeta potentials of the individual mineral- and oil-brine interfaces. In this section, we tune the model to the experimental data of Jackson et al., (2016) and Collini et al., (2020) to determine the magnitude and polarity of the micro-scale oil-brine zeta potential, as it was not possible to directly measure this in their experiments.

For a given experiment, we take the measured values of S_{wiry} ; S_{wi} ; S_{or} ; $\zeta_{mb}(S_w = 1)$ and I_w and adjust the values of the critical capillary radii r_{min} ; r_{Swiry} ; r_{Swi} ; r_{Sor} and r_{max} to develop a mixed-wet model bespoke to that experiment. The only model parameter that was not experimentally measured was the micro-scale oil-brine zeta potential, ζ_{ob} , so we tune this value such that the model macro-scale zeta potential matches the measured macro-scale zeta potential at $S_w = 1 - S_{or}$ (see selected examples in Figure 6; one for each oil used across the two experimental studies). Note that the sample of Oil D used by Jackson et al. (2016) [18] was different to the sample of Oil D used by [29] so we distinguish these here as Oil D(J) and Oil D(C) respectively.

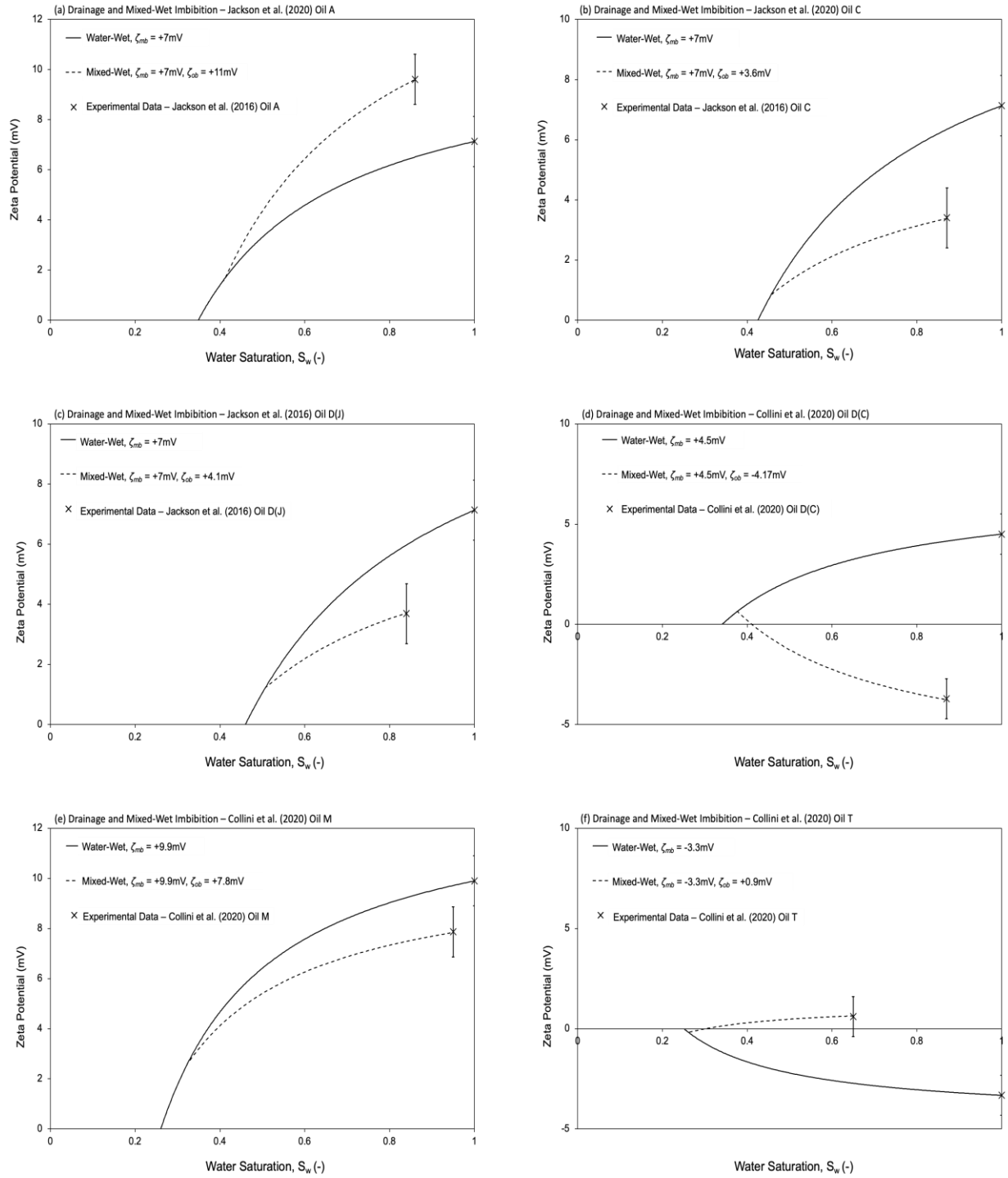


Figure 6 – Water-wet drainage (solid black lines) and mixed-wet imbibition (dashed lines) models showing macro-scale zeta potential as a function of water saturation S_w , compared against experimentally measured macro-scale zeta potential from (a) Jackson et al. (2016) [18] Oil A; (b) Jackson et al. (2016) [18] Oil C; (c) Jackson et al. (2016) [18] Oil D(J); (d) Collini et al. (2020) [29] Oil D(C); (e) Collini et al. (2020) [29] Oil M; (f) Collini et al. (2020) [29] Oil T. The model properties were adjusted in each case to match the measured S_{wirr} , S_{wis} , I_w and ζ_{mb} ($S_w = 1$) and the unknown value of micro-scale oil-brine zeta potential ζ_{ob} was tuned such that the model macro-scale zeta potential matches the experimentally measured macro-scale zeta potential at $S_w = 1 - S_{or}$.

The value of the micro-scale oil-brine zeta potential determined using this approach for all experiments reported by Jackson et al. (2016) [18] and Collini et al. (2020) [29] is shown in Figure 7.

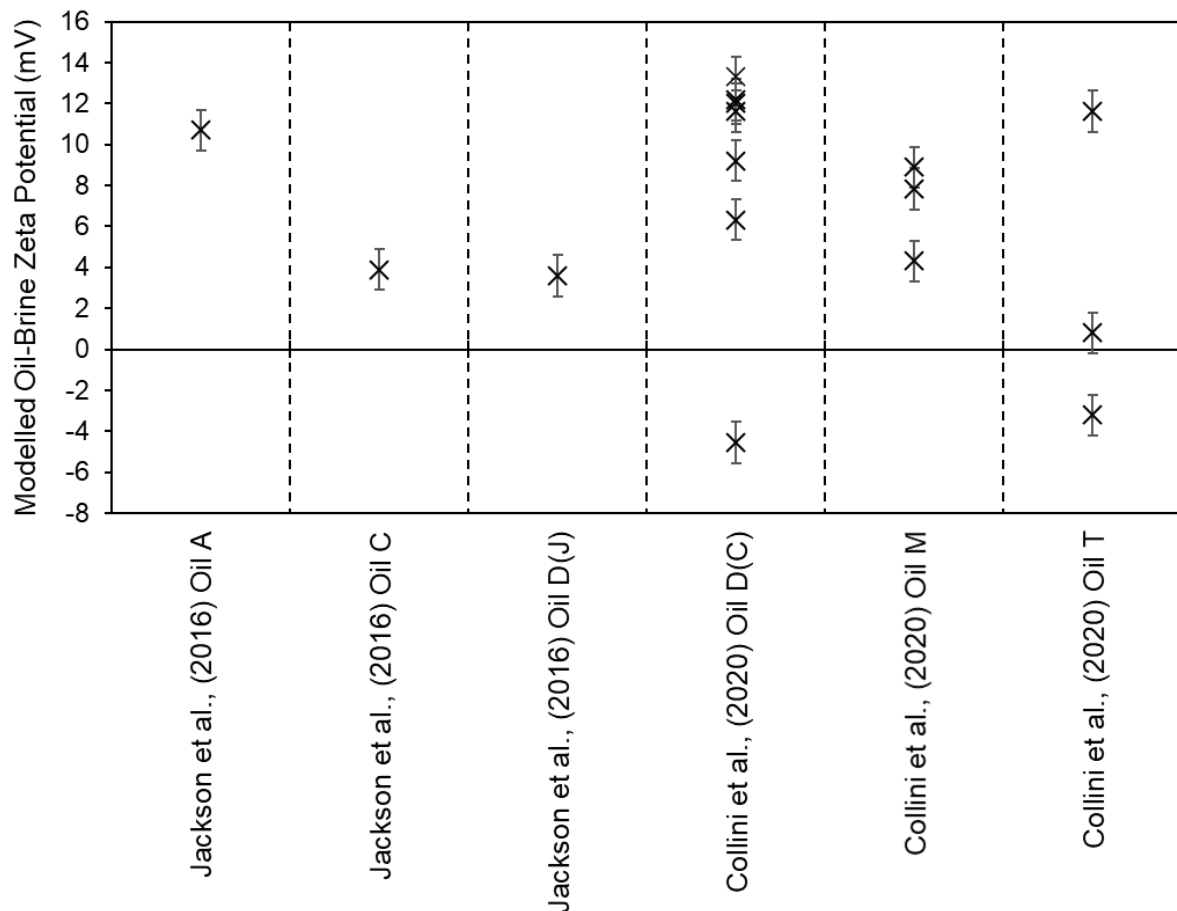


Figure 7 – Modelled micro-scale oil-brine zeta potential values for the different crude oils tested by Jackson et al., (2016) [18] and Collini et al., (2020) [29]. Different datapoints for a given crude oil correspond to experiments using different rock samples, brine compositions or temperature. 16 values of oil-brine zeta potential are reported in total.

The capillary tubes model suggests positive values for the micro-scale oil-brine zeta potential in most of the experiments tested, up to a maximum of +13.1mV (determined for the Oil D(C) experiment reported by Collini et al. (2020) [29] with carbonate sample BA at ambient laboratory temperature). Only two experiments, using crude oils D(C) and T, are interpreted to have negative micro-scale oil-brine zeta potential (determined for the Oil D(C) experiment reported by Collini et al., (2020) [29] with carbonate sample BD at 80 °C and the oil T experiment with sample TE at ambient temperature) with a minimum value of -4.1mV. The spread of oil-brine zeta potential values interpreted here is not surprising given the range of brine compositions and temperatures tested in the experiments, but the fact that the zeta potentials are mostly positive is unexpected.

As discussed previously, the polarity of the oil-brine zeta potential in Jackson and co-worker's experiments was interpreted using a very simple, qualitative approach: if the macro-scale zeta potential became more positive after aging then the micro-scale oil-brine zeta potential was interpreted to be positive, and *vice-versa*. In the 16 experiments conducted using high salinity formation brine, the crude oils tested were interpreted to have a positive oil-brine zeta potential in nine experiments and a negative oil-brine zeta potential in seven experiments (see Table 2 in [29]). However, in five of the seven experiments in which a negative macro-scale zeta potential was interpreted, it was noted that the micro-scale oil-brine zeta potential was not unambiguously negative; it could be positive but have smaller magnitude than the (positive) mineral-brine zeta potential [29]. In these experiments, the macro-scale zeta potential after aging remained positive but became smaller in magnitude after aging.

The micro-scale oil-brine zeta potential in the five ambiguous experiments were interpreted to be negative [29], but the model here instead predicts a positive oil-brine zeta potential that is smaller in magnitude than the mineral-brine zeta potential. Hence, the model only predicts a negative oil-brine zeta potential in two of the experiments. The polarity of the modelled oil-brine zeta potential obtained here is consistent with the polarity interpretations only when these were unambiguous [18, 29]. We return to this issue and its importance for predicting oil recovery during CSW in the discussion.

3.4. Link Between Macro-Scale Zeta Potential and Wettability

We finish by applying the capillary tubes model to investigate the link between the measured sample wettability, and the measured change in sample (macro-scale) zeta potential caused by wettability alteration ($\Delta\zeta_{wet}$), after aging in crude oil. We compare the model predictions to the experimental data shown in Figure 1. We use a single representative model with $S_{wirr} = 0.3$, $S_{wi} = 0.33$, $S_{or} = 0.9$; these values are broadly consistent with the experimental data. We assume the micro-scale mineral-brine zeta potential ζ_{mb} is positive, consistent with the model results reported in previous sections and the use of carbonate rock samples in the experiments, and consider three scenarios for the micro-scale oil-brine zeta potential: (i) the oil-brine interface is of the same polarity as the mineral-brine interface but greater in magnitude ($\zeta_{ob} > \zeta_{mb}$); (ii) the oil-brine interface is of the same polarity as the mineral-brine interface but smaller in magnitude ($\zeta_{ob} < \zeta_{mb}$), and (iii) the oil-brine interface has opposite polarity. The model results are shown in Figure 8 along with the experimental data re-plotted from Figure 1.

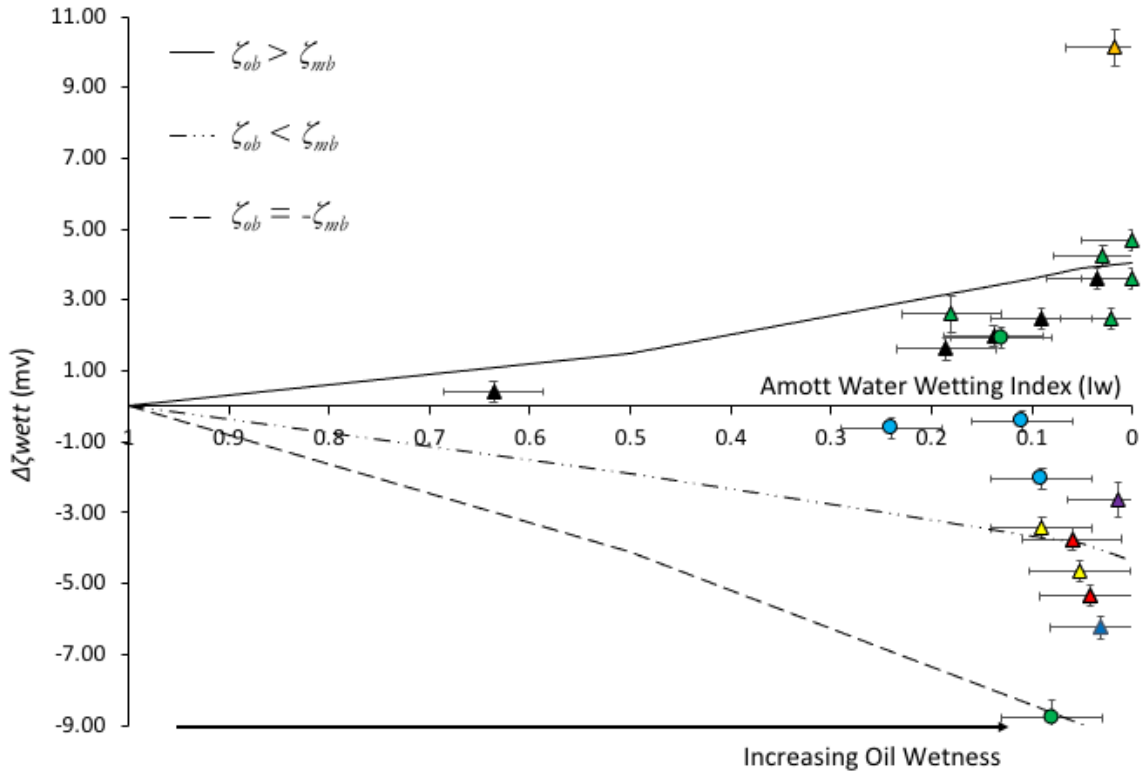


Figure 8 – Change in macro-scale zeta potential before and after aging and wettability alteration, $\Delta\zeta_{wett}$, as a function of Amott Water Wetting Index, I_w . Model uses $S_{wirr} = 0.3$, $S_{wi} = 0.33$, $S_{or} = 0.1$ and a positive micro-scale mineral-brine zeta potential ζ_{mb} . Points correspond to experimental data from [29] as reported in Figure 1 showing the change in macro-scale zeta potential measured on intact natural carbonate cores after drainage and aging with crude oil. Triangles represent measurements made at room temperature and circles represent measurements made at elevated reservoir temperature $>70^\circ\text{C}$. Different colours represent different crude oils.

The model broadly captures the observed trends in the experimental data: when the micro-scale oil-brine zeta potential is more positive than the mineral-brine zeta potential, the macro-scale zeta potential becomes relatively more positive with increasing oil-wetness; conversely, if the micro-scale oil-brine zeta potential is less positive, the macro-scale zeta potential becomes relatively less positive with increasing oil-wetness. If the polarity of the micro-scale oil-brine zeta potential is negative, then the macro-scale zeta potential becomes relatively less positive with increasing oil-wetness but is more negative for a given wettability and may invert to return a negative value if the model is sufficiently oil-wet. If we were to assume a negative value for the micro-scale mineral-brine interface, the same general trends would still be observed but with the polarity inverted.

Although the model captures the overall trends, it fails to quantitatively match the experimental data. The model predicts a close to linear trend between $\Delta\zeta_{wett}$ and I_w irrespective of the value of micro-scale oil-brine or mineral-brine zeta potential, whereas the experimental data exhibit a trend more comparable to a linear-log relationship. The model overpredicts the change in macro-scale

zeta potential in the mixed-wet regime ($0.1 < I_w < 0.8$) and does not reproduce the sharp changes in $\Delta\zeta_{wet}$ in the strongly oil-wet region ($I_w < 0.1$). The limitations of the model that may be responsible for these discrepancies and their implications for understanding the link between macro-scale zeta potential and wettability of porous media are discussed further in the next section.

4. Discussion

The bundle of capillary tubes model presented here reports, for the first time, a quantitative relationship between the macro (continuum)-scale zeta potential interpreted from streaming potential measurements on intact porous media, and changes in the wetting state of the mineral surfaces. The model is simplistic in its representation of rock pore-space but serves as a foundation from which to develop more advanced models and yields a number of insights into the relationship between zeta potential and wettability.

When water is strongly wetting, the macro-scale zeta potential of the porous medium reflects the micro-scale zeta potential of the mineral-brine interface, whereas when oil is strongly wetting, the macro-scale zeta potential reflects the micro-scale zeta potential of the oil-brine interface (Figure 4). Mixed-wet porous media yield a macro-scale zeta potential that is a combination of the micro-scale zeta potentials of both the mineral- and oil-brine interfaces, and which increasingly reflects the micro-scale zeta potential of the oil-brine interface as the porous medium becomes increasingly oil-wet, and *vice-versa* (Figure 5). If the micro-scale zeta potential of the oil-brine interface is of the same polarity but larger in magnitude than the micro-scale zeta potential of the mineral-brine interface, then the macro-scale zeta potential increases in magnitude with increasing oil-wetness, and *vice-versa*. If the polarities of the micro-scale oil-brine and mineral-brine interfaces are opposed, then inversion of the macro-scale zeta potential can occur with sufficient oil-wetness. These observations have been previously hypothesised based on qualitative interpretations of experimental data [18, 29, 30] but have not been supported by pore-scale modelling until now.

The zeta potential of the oil-brine interface has gained significant recent attention due to its importance in improved oil recovery (IOR) by controlled salinity waterflooding (CSW). In the carbonate rock samples tested by [18] and [29], brine dilution during conventional CSW yielded a more negative micro-scale mineral-brine zeta potential and IOR was observed only when the micro-scale oil-brine zeta potential was interpreted to be negative. When the oil-brine interface was interpreted to be positive, no IOR was observed during conventional CSW. Conversely, when the micro-scale oil-brine zeta potential was interpreted to be positive, IOR was only observed by

1 increasing brine salinity in an inverse CSW, causing the mineral-brine zeta potential to become
2 more positive. The capillary tubes model presented here predicts a positive oil-brine zeta potential
3 in most of the experiments reported by [18] and [29] (Figure 7).

4
5 Confirming the interpretations of the oil-brine zeta potential reported here with independent
6 experimental measurements is challenging. Most published data for the oil-brine zeta potential
7 were obtained using the EPM and oil-brine emulsions in simple, low ionic strength brines ($<0.1\text{M}$)
8 at laboratory temperature [34, 35, 69-71]. These are far from the experimental conditions used by
9 [18] and [29] or that are relevant in natural systems. The widely held belief that the oil-brine zeta
10 potential is negative is based on these studies. Acquiring relevant data in high ionic strength brines
11 and/or at elevated temperature using the EPM may never be possible because the oil-brine
12 emulsions are unstable, and the measured electrophoretic signals are very small. There are limited
13 data obtained using the EPM that approach relevant natural conditions and these suggest the oil-
14 brine zeta potential is indeed positive at $\text{pH} > 5$ in the presence of divalent ions such as Ca^{2+} ,
15 consistent with our model predictions: positive oil-brine zeta potential measurements with values
16 of ζ_{ob} between +2 and +14.7 mV in the presence of 50,000 ppm CaCl_2 (0.45M) and pH range 4-7
17 have been reported [35, 72], whilst a constant oil-brine zeta potential of +6 mV above 1M MgCl_2
18 was also reported [73].

19
20 Surface complexation models for the oil-brine interface suggest that divalent cations such as
21 calcium can interact with negatively charged carboxylic acid species in the crude oil to form
22 positively charged acid-cations complexes and yield an overall positive charge at the oil-brine
23 interface [74, 75]. The oil-brine zeta potential values predicted by our model (Figure 7) fall within
24 the ranges reported in independent experimental measurements in the presence of high calcium
25 concentrations. We suggest that the oil-brine zeta potential is more commonly positive than has
26 previously been thought and also note that electrophoretic measurements obtained on oil-brine
27 emulsions may not be representative of those in the subsurface as a further limitation. The many
28 published examples of CSW where the injection brine was diluted, and no additional oil recovery
29 was observed may have contained an unknown positively charged oil.

30
31 The model also provides insight into the relationship between macro-scale zeta potential and the
32 wettability of the porous medium, which may be useful in developing a tool to determine reservoir
33 wettability *in-situ* by measuring the zeta potential via downhole measurements of the streaming
34 potential, obtained using a wireline tool such as a Modular Formation Dynamics Tester. Two

probes equipped with pressure transducers and suitable non-polarising electrodes could be used to impose flow in the reservoir and measure the resulting pressure and voltage differences [76]. From these data, supplemented by measurements of the rock and formation brine conductivity, the zeta potential of the reservoir rocks in-situ could be determined. If a robust correlation between zeta potential and wettability can be identified, then the in-situ wettability could also be characterised [1, 30, 37].

The model captures the overall trend between zeta potential and wettability observed experimentally, but deviates in the mixed wet regime, where it tends to overpredict the change in zeta potential $\Delta\zeta_{wett}$ for a given wettability I_w , and does not capture the sharp changes in $\Delta\zeta_{wett}$ with small changes in I_w in strongly oil-wet conditions. This discrepancy may be due to the way in which we account for wettability. We assume that oil in water-wet capillaries is completely displaced during imbibition when, in natural rocks, water enters pores by thickening the wetting water film and trapping oil droplets or ganglia in the pore centres. Since we do not account for trapped oil, we may be underpredicting the number of water-wet pores for a given I_w , particularly in the mixed wet regime (Figure 8). Moreover, I_w may not be the best measure of wettability, as it characterises wettability using rock samples at the cm - m scale yet many of the mineral scale properties and mechanisms that control wettability and development of the electrical double layer occur at the sub nm scale. Characterising wettability across scales is a common and persistent problem for understanding multiphase flow. The sharp changes in zeta potential observed in response to very small changes in I_w in strongly oil wet samples suggest that important physical changes are occurring at the mineral-surface scale that have a strong effect on the macro-scale zeta potential but are not captured by macro-scale changes in I_w .

5. Conclusions

Motivated by the interpretation of experimental measurements of zeta potential in intact porous media [18, 29, 30] we report the first pore-scale model linking measured, macro-scale zeta potential with the micro-scale zeta potential on individual mineral surfaces. The micro-scale zeta potential depends on whether a mineral surface is water- or oil-wet: water-wet surfaces are assigned the mineral-brine zeta potential, but oil-wet surfaces are assigned the oil-brine zeta potential [18]. We model the pore-space as a bundle of capillary tubes of varying size which allows us to derive expressions for macro-scale zeta potential, brine saturation and wettability from first principles without the need for numerical modelling. Despite its simplicity, we show that the model captures experimentally measured relationships between macro-scale zeta potential and water saturation in

1 water-wet intact carbonate rocks [36]. We applied the model to determine the relationship
2 between macro-scale zeta potential and water saturation for different macro-scale wetting states,
3 and the relationship between macro-scale zeta potential and wettability at the residual oil
4 saturation, to interpret experimentally measured data on intact carbonate rock samples [18, 29, 30].
5

6 Regardless of wettability, the model predicts that the macro-scale zeta potential decreases with
7 decreasing water saturation, falling to zero at the irreducible water saturation when there is no flow
8 of water, consistent with experimental data from intact sandstone and carbonate samples [36, 37].
9 In water-wet models, the macro-scale zeta potential measured at full water saturation corresponds
10 to the micro-scale zeta potential of the mineral-brine interface, confirming the use of the streaming
11 potential method to determine micro-scale zeta potential of intact porous samples [1, 18, 29, 30-
12 32]. Moreover, the saturation-dependence of the macro-scale zeta potential is the same
13 irrespective of whether the water saturation is decreasing (drainage) or increasing (imbibition).
14

15 Wettability alteration leads to hysteretic behaviour in the saturation-dependence of the macro-
16 scale zeta potential because mineral surfaces that becomes oil-wet after drainage return the micro-
17 scale zeta potential of the oil-brine interface. Moreover, the macro-scale zeta potential exhibits a
18 clear relationship with wettability, because wettability reflects the ratio of water-wet to oil-wet
19 surfaces (pores). Such a quantitative relationship provides a basis to develop a downhole tool to
20 measure wettability *in-situ* [76].
21

22 The magnitude and polarity of the oil-brine zeta potential is difficult to measure at subsurface
23 conditions of high brine salinity and temperature. Fitting our model to experimental data obtained
24 on carbonate core samples allows the micro-scale oil-brine zeta potentials in these experiments to
25 be estimated, returning values between -4.1mV and +13.9mV despite the relatively high pH of 6-
26 7 [18, 29]. These results suggest that the oil-brine zeta potential is positive in many cases relevant
27 to subsurface reservoirs, when it has been previously assumed to be negative above pH approx. =
28 5 [20, 35, 38, 61 70-72]. A positive oil-brine zeta potential has important implications for surface
29 complexation models of the crude oil surface [74, 75, 77] and for the design of controlled salinity
30 waterflooding in oil reservoirs [29, 34, 38, 78].
31

32 The model predicts a clear relationship between zeta potential and wettability but does not
33 perfectly match experimental data, particularly in the mixed-wet regime. This is unsurprising given

1 the simplified representation of the pore space, but the work provides a foundation for the
2 development of more complex pore-scale models [13, 14, 53].
3

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