Comment on “Characterization of multi-phase electrokinetic coupling using a bundle of capillary tubes model” by Mathew Jackson

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1. Introduction

Jackson [2008] (hereafter referred to as J08) has developed a bundle-of-capillary-tubes model to describe multi-phase electrokinetic coupling. Part of J08 is based on the erroneous assumption that excess charge in the diffuse Gouy-Chapman double layer per unit capillary volume is constant for a given phase regardless of the capillary radius. This assumption leads to inconsistent and misleading results, because this excess charge density must scale with the inverse of capillary radius in the same manner as surface conduction does; this latter aspect is handled correctly by J08. For a capillary-tubes model, both the total excess charge per unit capillary volume (including the Stern and Gouy-Chapman layers) and the surface conductivity are proportional to the specific internal surface area [Johnson et al., 1986; Revil et al., 1998]. J08 makes the reasonable assumption that the thickness of the double layer is negligible compared with the capillary radius [Pride, 1994], which implies that the excess charge transported within the Gouy-Chapman layer alone (i.e., the excess charge responsible for electrokinetic phenomena) is also proportional to the specific internal surface area. Pride [1994] states that the Debye length associated with the diffuse double layer is generally smaller than 3
\[ \times 10^{-8} \text{ m}, \text{ which is significantly smaller than the grain size associated with most geological materials.} \]

Linde et al. [2007] and Revil et al. [2007] developed a representative elementary volume (REV) model for predicting electrokinetic coupling phenomena in an unsaturated water-wet media with air as the non-wetting phase. They demonstrated that their REV model was consistent with laboratory observations. Their model was based on the first-order assumption that the effective excess charge in the Gouy-Chapman layer per unit volume of water scaled with the inverse of water saturation.

One advantage of representing the pore space as a bundle of capillary tubes compared with an REV model is that the relative contribution of each capillary to the overall permeability of each phase can be determined at any water saturation, which makes it possible to develop a more accurate scaling relation than the one proposed by Linde et al. [2007] and Revil et al. [2007]. In this comment, I reformulate the key expression of J08 (i.e., his equation 21) by computing an effective excess charge in each polar phase at a given saturation by weighting, for each capillary, the excess charge in the Gouy-Chapman layer per unit capillary volume with the capillary’s relative contribution to permeability.

2. A Corrected Capillary Tubes Model

In the following, I develop a corrected capillary tubes model that does not suffer from the limitations and inconsistencies of the model proposed by J08 (see Table 1, mostly extracted from J08, for the definition of the symbols used).
The excess charge in the Gouy-Chapman layer per unit capillary volume \( Q(r_c) \) is for the wetting fluid given by (c.f., equation 14 in J08 for surface conductivity)

\[
Q(r_c) = Q_{sw} \frac{2 \pi r_c}{\pi r_c^2} = Q_{sw} \frac{2}{r_c},
\]

(1)

where \( Q_{sw} \) is the specific excess surface charge in the Gouy-Chapman layer for the wetting phase. For capillaries filled with a non-wetting polar fluid, \( Q_{sw} \) needs to be replaced by \( Q_{snw} \). To calculate the effective excess charge at full water saturation, it is necessary to weight the excess charge in each capillary with its contribution to permeability, and hence flow, by combining equation 1 with equation (10) in J08, which yields

\[
Q_w(S_w = 1) = 2Q_{sw} \frac{\int_{r_{min}}^{r_{max}} r_c^3 n(r_c) dr_c}{\int_{r_{min}}^{r_{max}} r_c^4 n(r_c) dr_c}.
\]

(2)

This corresponds to the \( Q_w \) that can be estimated from measurements of the streaming potential coupling coefficient at full water saturation (see equation 23 in J08). The corresponding relative excess charge per unit saturated volume for the water-wet case \( Q_{rw}(S_w) \) is given by

\[
Q_{rw}(S_w) = \frac{\int_{r_{min}}^{r_{max}} r_c^3 n(r_c) dr_c}{\int_{r_{min}}^{r_{max}} r_c^4 n(r_c) dr_c} \frac{\int_{r_{min}}^{r_{max}} r_c^3 n(r_c) dr_c}{\int_{r_{min}}^{r_{max}} r_c^4 n(r_c) dr_c}.
\]

(3)

Figure 1a shows how \( Q_{rw}(S_w) \) increases with a decreasing water saturation for different values of \( m \) (see equation 30 in J08). This behavior is intuitively obvious, since at decreasing water saturations, the relative contribution of smaller capillaries to flow is increasing and \( Q(r_c) \) is higher for smaller capillaries than for larger capillaries (see equation 1). J08 assumes that \( Q_{rw}(S_w)=1 \) (i.e., the dotted line in Figure 1a), which is
clearly incorrect. For comparison, Figure 1a also displays the model of Linde et al. [2007], in which it is assumed that

$$Q_{rw}(S_w) = \frac{Q_w(S_w = 1)}{S_w}. \quad (4)$$

Since $Q_{rw}(S_w)$ is varying, the expression for the relative streaming potential coupling coefficient at partial saturation is given by (c.f., equation 26 in J08)

$$C_r(S_w) = \frac{k_{rw}(S_w)Q_{rw}(S_w)}{\sigma_r(S_w)}. \quad (5)$$

The relative excess charge for the oil-wet case with a non-polar oil $Q_{rnw}(S_w)$ is then given by

$$Q_{rnw}(S_w) = \frac{\int_{r_{min}}^{r_{max}} r_c^3 n(rc) dr_c}{\int_{r_{min}}^{r_{max}} r_c^3 n(rc) dr_c}. \quad (6)$$

The predicted behavior of the relative streaming potential coupling coefficient for the oil-wet case is shown in Figure 1b. In contrast to the water-wet case, $Q_{rnw}(S_w) \leq 1$ and $Q_{rnw}(S_w)$ decreases with decreasing water saturation. This behavior is also intuitive, since no water flow takes place in the smaller capillaries in which $Q(rc)$ is high. The behavior predicted in Figure 1 is only caused by geometrical effects.

By replacing the constant $Q_w$ and $Q_{nw}$ of J08 with the new expression for the volumetric excess charge (equation 1 above), the general expression for the streaming potential coupling coefficient is (c.f., equation (21) in J08)
\[ C = \left[ \frac{Q_{nw}}{\mu_{nw}} \int_{r_{nw}}^{r_{max}} r_c^2 n(r_c) dr_c + \frac{Q_{sw}}{\mu_{sw}} \int_{r_{sw}}^{r_{max}} r_c^3 n(r_c) dr_c \right] \]

\[ (7) \quad \left\{ \left[ \sigma_{nw} \int_{r_{nw}}^{r_{max}} r_c^2 n(r_c) dr_c + 2\sigma_{sw} \int_{r_{sw}}^{r_{max}} r_c n(r_c) dr_c + \sigma_{sw} \int_{r_{sw}}^{r_{max}} r_c^2 n(r_c) dr_c + 2\sigma_{sw} \int_{r_{sw}}^{r_{max}} r_c n(r_c) dr_c \right] \right\}^1 \]

3. Implications of J08's erroneous assumption

J08’s erroneous assumption that the relative excess charge density is constant for variable saturations leads J08 to make the following conclusions:

- The relative streaming potential coupling coefficient for water-wet capillaries \( C_r \) is given by the model of Perrier and Morat [2000], where \( C_r \) is the ratio between the relative permeability and the relative electrical conductivity.

- \( C_r \) for oil-wet capillaries occupied by water and a non-polar oil is significantly larger than unity at relatively low water saturations.

In contrast, the corrected model presented below results in the following conclusions:

- \( C_r \) for water-wet capillaries falls between the model of Perrier and Morat [2000] and that of Linde et al. [2007] and Revil et al. [2007], implying that a very detailed model of the pore structure is needed to make quantitative use of self-potential data under general multi-phase conditions.

- For laboratory data, the corrected model and the model of Revil et al. [2007] are very similar, with both matching the data better than J08’s model regardless of the choice of the parameter \( m \) that describes the pore-size distribution.

- For oil-wet capillaries occupied by water and a non-polar oil, increases in \( C_r \) with decreasing water saturation are less important than predicted by J08 and that the highest \( C_r \) occurs at higher water saturations.
4. Implications for Water-Wet and Oil-Wet Media

For brevity, I only compare the predicted relative streaming potential coupling coefficients for some of the examples treated by J08, namely those for which the irreducible water saturation is 0.05.

Figure 2a shows the predicted $C_r$ for water-wet capillaries occupied by water and a non-wetting nonpolar second phase for which $S_{w irr}=0.05$ and bulk electrical conductivity dominates. Figure 2b shows the corresponding plot for which surface electrical conductivity dominates (c.f., Figure 4b in J08). Compared to J08, the corrected model predicts significantly smaller decreases of $C_r$ with decreasing water saturations, regardless of the dominant conduction mechanism.

Figure 3 displays $C_r$ as a function of water saturation for the models of Revil et al. [2007], J08, and the corrected model presented here together with experimental data on a dolomite sample presented in Figure 6 of Revil et al. [2007]. The corrected capillary tube model with $m=12$ predicts behavior very similar to that of the Revil et al. [2007] model, whereas J08's model increasingly underestimates the relative coupling coefficient at low water saturations. The weighted root mean square error (RMSE) of the model of Revil et al. [2007] is 1.13, the weighted RMSE of the corrected capillary tube model is 1.28, and the weighted RMSE of J08’s model is 1.56. The parameters of the relative permeability and relative electrical conductivity functions were independently evaluated as described in Revil et al. [2007] and are identical to those used by J08. The parameter $m$ is here only used to calculate $Q_{rw}(S_w)$ (equation 3) needed to calculate $C_r(S_w)$ (equation 5). The
corrected model fits the experimental data better than J08’s model for all values of $m$
considered by J08.

J08 also considered the case of oil-wet capillaries filled with water and nonpolar oil
for which the smallest capillaries are water filled $S_{nwwirr}$. For the case in which bulk
electrical conductivity dominates (Figure 2c) and $S_{nwwirr}=0.05$, the predicted increase in
$C_r$ at moderate saturations compared with full water saturation is approximately three
times less important than predicted by J08 (c.f., Figure 5b in J08). Furthermore, the peak
is shifted towards higher water saturations. A similar difference is observed for cases in
which surface electrical conductivity is the dominant conduction mechanism. This
implies that temporal variations in self-potential signals associated with oil-recovery in
oil-wet media are smaller than those predicted by J08. Laboratory and field-scale
experiments of oil-wet media filled with water and nonpolar oil must be carried out
before the validity of this theory can be established.

5. Concluding Remarks

J08 states that the capillary tubes model can be used to identify fundamental
relationships between $C_r$ and other macroscopic transport parameters. By making the
non-physical assumption that $Q_w(S_w)=1$, he came to the incorrect conclusion that the
relationship proposed by Perrier and Morat [2000] is valid. For the corrected capillary
tubes model presented here, the predicted behavior for the $C_r$ in the water-wet case falls
between the model of Perrier and Morat [2000] and the one of Linde et al. [2007] and
Revil et al. [2007]. For accurate modeling of electrokinetic phenomena at low water
saturations in real geological media, a realistic pore network model would be necessary to
accurately determine $Q_{nw}(S_w)$. Such models should not only incorporate geometrical scaling, but also express $Q_{sw}$ as a function of mineral fractions and their respective grain size distributions.

J08 also treats the case of oil-wet capillaries occupied by water and a nonpolar oil. The corrected capillary tubes model predicts $C_r$ above 1 at moderate water saturations, as predicted by J08, but the relative increase is much smaller and the peak occurs at higher water saturations. Laboratory experiments are needed to assess the validity of this model for oil-wet media.

**Acknowledgements.** I want to thank A. Revil for many illuminating discussions about electrokinetic phenomena. I also thank Alan Green and Stewart Greenhalgh for commenting on draft versions of this comment. Two anonymous reviews helped to improve the quality of this comment. Matthew Jackson corrected an error in my original equation 1 where the tortuosity $t$ ($t=1$ for all examples considered in this comment and J08) appeared in the denominator.

**REFERENCES**


Figure 1. (a) The relative excess charge per unit water saturated volume as a function of water saturation for a water-wet bundle of capillary tubes occupied by water and a non-polar phase for different capillary radii distributions. (b) The corresponding relationship for an oil-wet bundle of capillary tubes occupied by water and a non-polar oil. Solid lines - cases where the excess charge in the Gouy-Chapman layer per unit capillary volume is dependent of capillary radii (this work); dotted lines - case treated by J08 for which the excess charge in the Gouy-Chapman layer per unit capillary volume is independent of capillary radii; dash-dotted line in (a) - model of Linde et al. [2007].
Figure 2. Relative streaming potential coupling coefficient $C_r$ as a function of water saturation for a water-wet bundle of capillary tubes occupied by water and a non-polar phase for different capillary radii distributions in which either (a) bulk electrical conductivity or (b) surface electrical conductivity dominates. The corresponding relationships for an oil-wet bundle of capillary tubes occupied by water and a non-polar oil are given in diagrams (c) and (d). Solid lines - cases for which the excess charge in the Gouy-Chapman layer per unit capillary volume is dependent of capillary radii (this work); dotted lines - denote the cases treated by J08 for which the excess charge in the Gouy-Chapman layer per unit capillary volume is independent of capillary radii.
Figure 3. Relative coupling coefficients as a function of water saturation predicted using this model (solid line), the model of Revil et al. (2007) (dash-dotted line), and the model of Perrier and Morat [2000] derived by J08 (dotted line) and measured experimentally by Revil et al. [2007] during primary drainage of water by nitrogen in a water-wet dolomite sample. Predicted curves are based on the assumption that relative electrical conductivity is given by Archie’s second law with $n=2.7$, and the water relative permeability is given by $k_{rw} = (S_w - S_{wirr})/(1-S_{wirr})^{(2+3)\lambda}$, with $S_{wirr} = 0.36$ and $\lambda = 0.87$. Values of $n$, $S_{wirr}$, and $\lambda$ were obtained by Revil et al. [2007] from their experimental data.
Table 1. Nomenclature.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Units</th>
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<tr>
<td>$A$</td>
<td>area</td>
<td>m²</td>
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<tr>
<td>$C_r$</td>
<td>relative streaming potential coupling coefficient</td>
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<td>$k_{nw}$</td>
<td>relative permeability of the wetting phase</td>
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<td>$\mu_w$</td>
<td>viscosity of the wetting phase</td>
<td>Pa s</td>
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<td>$\mu_{nw}$</td>
<td>viscosity of the non-wetting phase</td>
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<td>$m$</td>
<td>parameter describing the pore-size distribution</td>
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<td>$n(r_c)$</td>
<td>number of capillary tubes of size $r_c$</td>
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<td>excess charge in the Gouy-Chapman layer per unit capillary volume</td>
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<td>specific excess surface charge in the Gouy-Chapman layer for the wetting phase</td>
<td>C m⁻¹</td>
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<td>$r_c$</td>
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<td>maximum capillary radius of wetting phase</td>
<td>m</td>
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