Electrokinetics in porous media
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Citation for published version (APA):
Luong, D. T. (2014). Electrokinetics in porous media

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Chapter 4

Examination of a theoretical model of streaming potential coupling coefficient

4.1 Introduction

Characterization of porous media and permeability dependence of the streaming potential coupling coefficient (SPCC) are studied in chapter 2 and chapter 3, respectively. In those chapters, the SPCC is experimentally measured and the zeta potential is deduced from that with knowledge of the electrical conductivity, viscosity and electrical permittivity of the fluid. That is the most commonly used approach to obtain the SPCC and the zeta potential of electrolyte saturated rocks. Glover et al. [27] developed a theoretical model to calculate the zeta potential and the SPCC of reservoir rocks and other porous media. By using reasonable values of input parameters that are supported by independent measurements or theory, Glover et al. [27] have obtained and compared the theoretical results to an experimental data set of 290 SPCC measurements and 269 zeta potential measurements using data from 29 publications. The comparison shows that the theoretical model can reproduce the main features of the experimental data.

However, the experimental data set was collected from different sources that may lead to a dissimilarity in fluid conductivity, in pH of pore fluid (a big range of pH from 5.5 to 11), in temperature and sample compositions. Some microstructure parameters that are needed to model were also not given in the original publications. The zeta potential and surface conductance themselves may be also different from
sample to sample [65]. Therefore, all those dissimilarities may cause the observed deviations.

In this chapter we want to examine how well the model works for 20 consolidated samples with 7 different concentrations of a NaCl solution and 9 different temperatures. To do so, firstly the SPCC and the zeta potential are experimentally measured as a function of the electrolyte concentration and temperature. Afterwards the model is used by taking fluid parameters, rock-fluid interface parameters already provided in [27] and rock microstructure parameters (porosity, permeability and formation factor) measured by ourselves for all samples. The proton surface conductance is adjusted to fit the experimental data. The comparisons are carried out for each sample.

For electrolyte concentration dependence of the SPCC, the comparison shows that the theoretical model is not in agreement with the experimental data, especially in low concentration range. However, if the zeta potential is considered to be constant over electrolyte concentration at fixed temperature the model fits the experimental data very well in a whole range of concentration. This leads to the suggestion that the formula of the zeta potential against electrolyte concentration in the model needs to be adjusted accordingly. Beside the model given in [27], we also use other empirical models from Pride and Morgan [66], Vinogradov et al. [67], Jaafar et al. [68] and Jouniaux and Ishido [69] to predict the SPCC as a function of electrolyte concentration. But none of them can fit experimental data at low electrolyte concentration. For temperature dependence of the SPCC, we implement a zeta potential offset to the model which improves the fit to experimental data. The comparison shows that the theoretical model does not fit the experimental data well but it can show the increase of the SPCC with increasing temperature as measured.

This chapter includes five sections. Section 4.2 describes the theoretical background of streaming potential including the calculation of the Stern potential, the zeta potential, fluid relative electric permittivity, fluid viscosity, fluid electrical conductivity and disassociation constant of water. Section 4.3 presents the experimental measurements. Section 4.4 contains the experimental results, discussion and comparisons between the experimental data and the results of the theoretical model. Conclusions are provided in Section 4.5.
4.2 Theoretical model of streaming potential

According to eq. (3.4), to model the SPCC one needs to know (1) the zeta potential, (2) the fluid relative electric permittivity, (3) the fluid viscosity, (4) the fluid electrical conductivity, (5) the surface conduction as a function of electrolyte concentration and temperature as well as the rock microstructure parameters such as permeability and formation factor. The surface conduction has already been described in chapter 3. For the zeta potential, the fluid relative electric permittivity, the fluid viscosity and the fluid electrical conductivity in electrolyte aqueous solutions as a function of electrolyte concentration and temperature, we use the model described by Glover et al. [27] and outlined as below:

Zeta potential

The electrical potential distribution \( \varphi \) in the EDL has, approximately, an exponential distribution given in [25–27]

\[
\varphi = \varphi_d \exp(-\chi/\chi_d), \tag{4.1}
\]

where \( \varphi_d \) is the Stern potential (V) that depends on the electrolyte concentration, pH, temperature and rock/fluid interface parameters and given by

\[
\varphi_d = \frac{2k_BT}{3e} \ln \left( \frac{\sqrt{8 \times 10^4 e \epsilon_0 k_BT N (10^{-pH} + K_M e C_f)}}{2 e \Gamma_s K_{(\omega)}} \right) \left[ \frac{C_f + 10^{-pH} + 10^pH - p_{Kw}}{\sqrt{C_f}} \right]. \tag{4.2}
\]

\( \chi_d \) is the Debye length (m) given in eq. (1.7) and is rewritten for 1:1 electrolyte as below

\[
\chi_d = \sqrt{\frac{e_0 \epsilon_\epsilon_0 k_BT}{2000 N e^2 C_f}}. \tag{4.3}
\]

\( \chi \) is the distance from the mineral surface. Eq. (4.2) and eq. (4.3) are valid for 1:1 electrolytes. Eq. (4.1) is, in fact, the solution of the linearized Poisson-Boltzmann equation describing the electrostatic potential distribution in the electrical double layer and is called the Debye-Hückel approximation [32]. The zeta potential can then be calculated as

\[
\zeta = \varphi_d \exp(-\chi/\chi_d). \tag{4.4}
\]
where $\chi = 2.4 \times 10^{-10}$ m is the shear plane distance (the distance from the mineral surface to the shear plane).

In eq. (4.2) and eq. (4.3), $k_b$ is the Boltzmann’s constant, $T$ is temperature (in K), $\epsilon_0$ is the dielectric permittivity in vacuum, $\epsilon_r$ is the relative permittivity, $e$ is the elementary charge, $N$ is the Avogadro’s number, $\text{pH}$ is the fluid pH, $K_{Me}$ is the binding constant for sodium adsorption, $K_{\text{dis}}$ is the disassociation constant for dehydrogenization of silanol surface sites, $\Gamma_s$ is the surface site density, $K_w$ is the disassociation constant of water and $C_f$ is the electrolyte concentration.

### Fluid relative electric permittivity

The value of $\epsilon_r$ is normally taken to be 80 for an aqueous solution at 25°C. However, Glover et al. [27] have taken into account the variation of the relative electric permittivity as a function of fluid electrolyte concentration and temperature using an empirical equation:

$$
\epsilon_r(T, C_f) = a_0 + a_1 T + a_2 T^2 + a_3 T^3 + c_1 C_f + c_2 C_f^2 + c_3 C_f^3,
$$

(4.5)

where $a_0 = 295.68$, $a_1 = -1.2283 \text{K}^{-1}$, $a_2 = 2.0941 \times 10^{-3} \text{K}^{-2}$, $a_3 = -1.41 \times 10^{-6} \text{K}^{-3}$, $c_1 = -13 \text{Lmol}^{-1}$, $c_2 = 1.065 (\text{Lmol}^{-1})^2$, $c_3 = -0.03006 (\text{Lmol}^{-1})^3$, $T$ is in Kelvin. The equation is valid in the range from 273K to 373K and $C_f$ is the electrolyte concentration in mol/L.

### Fluid viscosity

The dynamic viscosity $\eta$ of the pore fluid (in Pa.s) is calculated using an empirical equation [70]:

$$
\eta(T, C_f) = e_1 + e_2 \text{exp}(\alpha_1 T) + e_3 \text{exp}(\alpha_2 C_f) + e_4 \text{exp}(\alpha_3 T + \alpha_4 C_f),
$$

(4.6)

where $e_1 = 4.95166 \times 10^{-5}$ Pa.s, $e_2 = 6.034658 \times 10^{-4}$ Pa.s, $e_3 = 9.703832 \times 10^{-4}$ Pa.s, $e_4 = 1.025107 \times 10^{-4}$ Pa.s, $\alpha_1 = -0.06653081/\text{°C}$, $\alpha_2 = -0.1447269/\text{molar}$, $\alpha_3 = -0.02062455/\text{°C}$, $\alpha_4 = -0.1301095/\text{molar}$. $T$ is in °C and $C_f$ is the electrolyte concentration in mol/L.
Fluid electrical conductivity

The fluid electrical conductivity (in S/m) is given in [27, 71] as a function of fluid concentration and temperature

$$\sigma_f(T, C_f) = (d_1 + d_2 T + d_3 T^2)C_f - \frac{d_4 + d_5 T}{1 + d_6 \sqrt{C_f}}C_f^{3/2},$$  \hspace{1cm} (4.7)

where $d_1 = 5.6$ (S.L/mol), $d_2 = 0.27$ (S.L/mol)/°C, $d_3 = -1.51 \times 10^{-4}$ (S.L/mol)/°C², $d_4 = 2.36$ (S/m/(mol/L)³/²), $d_5 = 0.099$ (S/m/(mol/L)³/²/°C), $d_6 = 0.214$ ((mol/L)⁻¹/²). $T$ is in °C and $C_f$ is the electrolyte concentration in mol/L.

Disassociation constant

This parameter defines the fluid pH which is required to calculate the Stern potential and the surface conductance. The value of $K_w$ varies with temperature and is approximately in the range of 0°C to 100°C as follows [54]

$$K_w = 6.9978 \times 10^{-16} + 5.0178 \times 10^{-16}T - 2.4434 \times 10^{-17}T^2 + 7.1948 \times 10^{-19}T^3$$ \hspace{1cm} (4.8)

where $T$ is in °C.

Indeed, the fluid pH is also defined by the reaction of water with carbon dioxide from the air which generates bicarbonate (HCO₃⁻) and hydrogen ions (H⁺) [27]. This leads to that water exposed to air is slightly acidic. In the model, one needs to know the pH to calculate the concentrations of hydrogen ions ($10^{-\text{pH}}$) and hydroxyl ions ($10^{\text{pH}-pK_w}$) in the fluid. The pH values required to model is directly measured by a pH meter.

4.3 Experiments

Streaming potential measurements have been performed on 20 consolidated samples (55 mm in length and 25 mm in diameter as shown in Fig. 4.1) including both natural and artificial samples from different sources. Beside 12 consolidated samples used in chapter 3 for the study of permeability dependence of the SPCC (see Table 3.1), we use 8 more samples for the experimental examination of the
Table 4.1: Sample ID, mineral composition and microstructure parameters of the samples. Symbols $k_o$ (in mD), $\phi$ (in %), $F$ (no units), $\alpha_\infty$ (no units), $\rho_s$ (in kg/m$^3$) stand for permeability, porosity, formation factor, tortuosity and solid density, respectively.

For lithology, EST stands for Estailhade limestone, IND stands for Indiana Limestone, BER stands for Berea sandstone, BEN stands for Bentheim sandstone.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Mineral composition</th>
<th>$k_o$ (mD)</th>
<th>$\phi$ (%)</th>
<th>$F$ (no units)</th>
<th>$\alpha_\infty$ (no units)</th>
<th>$\rho_s$ (kg/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>EST Mostlly Calcite (see [72])</td>
<td>294</td>
<td>31.5</td>
<td>9.0</td>
<td>2.8</td>
<td>2705</td>
</tr>
<tr>
<td>2</td>
<td>IND01 Mostly Calcite, Silica, Alumina, Magnesium carbonate (see [73, 74])</td>
<td>103</td>
<td>20.0</td>
<td>32.0</td>
<td>6.4</td>
<td>2745</td>
</tr>
<tr>
<td>3</td>
<td>BER5 Silica (74.0-98.0%), Alumina and clays (see [60, 74])</td>
<td>51</td>
<td>21.1</td>
<td>14.5</td>
<td>3.1</td>
<td>2726</td>
</tr>
<tr>
<td>4</td>
<td>BER12</td>
<td>-</td>
<td>48</td>
<td>22.9</td>
<td>14.0</td>
<td>3.2</td>
</tr>
<tr>
<td>5</td>
<td>BER502</td>
<td>-</td>
<td>182</td>
<td>22.5</td>
<td>13.5</td>
<td>3.0</td>
</tr>
<tr>
<td>6</td>
<td>BER11</td>
<td>-</td>
<td>170</td>
<td>21.1</td>
<td>14.0</td>
<td>3.4</td>
</tr>
<tr>
<td>7</td>
<td>BEN6 Mostly Silica (see [75])</td>
<td>1382</td>
<td>22.3</td>
<td>12.0</td>
<td>2.7</td>
<td>2638</td>
</tr>
<tr>
<td>8</td>
<td>BEN7 Mostly Silica (see [75])</td>
<td>1438</td>
<td>22.2</td>
<td>12.6</td>
<td>2.8</td>
<td>2647</td>
</tr>
</tbody>
</table>

Figure 4.1: Consolidated samples

model. The natural samples numbered from 1 to 7 are obtained from Shell company [76]. The last one numbered 8 is obtained from Delft University [77]. The mineral composition and microstructure parameters of the samples are also shown in the Table 4.1.

The experimental setup for the streaming potential measurement as a function of electrolyte concentrations (at temperature 22 ± 1°C) as well as the way to measure the porosity, solid density, permeability and formation factor are well described in chapter 3. For measuring the streaming potential as a function of temperature, we immerse the core holder and the bottle containing the solution into the bath
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Figure 4.2: The main part of the setup for streaming potential measurements as a function of temperature. 1, Core holder; 2, Ag/AgCl electrodes; 3, Solution container; 4, Tubing used to pump the solution from the container; 5, Tubing connecting the pump outlet and the core holder inlet; 6, Tubing for recirculation; 7, Shield cable for electrical potential measurements.

Table 4.2: The streaming potential coupling coefficient (in mV/bar) for different electrolyte concentrations of $4 \times 10^{-4}$ M, $10^{-3}$ M, $2.5 \times 10^{-3}$ M, $5.0 \times 10^{-3}$ M, $10^{-2}$ M, $2.0 \times 10^{-2}$ M and $5.0 \times 10^{-2}$ M, respectively.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>0.4 mM</th>
<th>1 mM</th>
<th>2.5 mM</th>
<th>5 mM</th>
<th>10 mM</th>
<th>20 mM</th>
<th>50 mM</th>
</tr>
</thead>
<tbody>
<tr>
<td>EST</td>
<td>-155.0</td>
<td>-86.0</td>
<td>-45.5</td>
<td>-23.0</td>
<td>-12.5</td>
<td>-6.8</td>
<td>-2.6</td>
</tr>
<tr>
<td>IND01</td>
<td>-68.0</td>
<td>-49.5</td>
<td>-25.0</td>
<td>-13.5</td>
<td>-7.6</td>
<td>-3.7</td>
<td>-1.8</td>
</tr>
<tr>
<td>BER5</td>
<td>-82.0</td>
<td>-56.0</td>
<td>-35.0</td>
<td>-21.0</td>
<td>-12.5</td>
<td>-7.0</td>
<td>-3.2</td>
</tr>
<tr>
<td>BER12</td>
<td>-94.0</td>
<td>-64.0</td>
<td>-36.0</td>
<td>-22.0</td>
<td>-13.0</td>
<td>-7.1</td>
<td>-3.3</td>
</tr>
<tr>
<td>BER502</td>
<td>-130.0</td>
<td>-85.0</td>
<td>-46.0</td>
<td>-24.5</td>
<td>-15.0</td>
<td>-8.5</td>
<td>-3.8</td>
</tr>
<tr>
<td>BER11</td>
<td>-180.0</td>
<td>-95.0</td>
<td>-55.0</td>
<td>-28.0</td>
<td>-17.0</td>
<td>-9.4</td>
<td>-4.4</td>
</tr>
<tr>
<td>BEN6</td>
<td>-480.0</td>
<td>-270.0</td>
<td>-105.0</td>
<td>-52.5</td>
<td>-27.0</td>
<td>-14.5</td>
<td>-6.1</td>
</tr>
<tr>
<td>BEN7</td>
<td>-550.0</td>
<td>-285.0</td>
<td>-110.0</td>
<td>-55.5</td>
<td>-28.0</td>
<td>-15.0</td>
<td>-6.7</td>
</tr>
</tbody>
</table>

of a thermally stabilized water bath (Thermo Fisher Scientific SC150 and A25) as shown in Fig. 4.2.

The solutions used in our measurements are NaCl solutions with 7 different concentrations ($4.0 \times 10^{-4}$ M, $1.0 \times 10^{-3}$ M, $2.5 \times 10^{-3}$ M, $5.0 \times 10^{-3}$ M, $1.0 \times 10^{-2}$ M, $2.0 \times 10^{-2}$ M and $5.0 \times 10^{-2}$ M). Temperatures used in our measurements are 6°C, 11°C, 16°C, 21°C, 26°C, 31°C, 36°C, 41°C and 46°C, respectively. It should be noted that the model presented in section 4.2 is valid in the range 0°C - 100°C [27].
4.4 Results and discussion

4.4.1 Porosity, solid density, permeability and formation factor

Porosity, density and permeability of the samples are shown in Table 3.1 and Table 4.1 with an error of 3%, 5% and 6% respectively. Values of the formation factor and corresponding tortuosity are also reported in Table 3.1 and Table 4.1 with an error of 6% and 9%, respectively.

4.4.2 Streaming potential as a function of electrolyte concentration

The way used to obtain the SPCC is the same as described in chapter 3. The SPCC at different electrolyte concentrations for all samples is shown in Table 3.2 and Table 4.2. The maximum error of the SPCC is 15%.

By using the input parameters presented by Glover et al. [27] in Table 3.3 except proton surface conductance $c_{Prot}$ which is adjusted to fit data as described in chapter 3, we have calculated the change of the zeta potential, the fluid viscosity, the relative permittivity, and the surface conduction against the electrolyte concentration.

According to Glover et al. [27], one can improve the fit of the model to the experimental data by introducing a constant zeta potential offset $\zeta_o$. It means that eq. (4.4) is replaced by $\zeta = \phi_d \exp(-\chi_{d}/\chi_d) + \zeta_o$. The zeta potential offset enables the model to reproduce the SPCC and zeta potential at high salinity. The physical meaning behind that is still unclear even the possible explanation is partially given in [27]. Therefore, more research needs to be implemented to understand that parameter.

The relationship between the electrolyte concentration and the fluid electrical conductivity is now needed for the model. This relationship is found by fitting experimental data as shown in Fig. 4.3 for the sample IND01, for example. Fig. 4.3 shows that the relationship follows $\sigma_f = 9.5C_f + 0.0085$ (S/m) for the sample IND01 and it is in good agreement with the model of Sen and Goode [71] for fluid electrical conductivity of a NaCl solution as a function of electrolyte concentration in the ranges $10^{-6} < C_f < 1M$ and $15^\circ C < T < 25^\circ C$ ($\sigma_f = 10C_f$). Similarly, the relationships between the electrolyte concentration and fluid electrical conductivity are obtained for other samples.
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Figure 4.3: Fluid electrical conductivity versus electrolyte concentration for sample IND01.

Figure 4.4: Measured and modeled results of the streaming potential coupling coefficient for IND01. Three pH values (6, 7 and 8), the zeta potential offset (\( \zeta_0 = 0.045 \text{V} \)) and the proton surface conductance \( c_{Prot} = 3 \times 10^{-28} \text{ S m}^2/\text{site} \) are used to model.

Figure 4.5: Zeta potential versus electrolyte concentration for sample BereaUS5.
Figure 4.6: (a) is for the IND01 sample with $c_{Pr} = 3 \times 10^{-28}$ S m$^2$/site, (b) is for the EST sample with $c_{Pr} = 9.6 \times 10^{-28}$ S m$^2$/site, (c) is for the BEN6 and BEN7 samples with $c_{Pr} = 3 \times 10^{-28}$ S m$^2$/site, (d) is for the set of BereaUS samples with $c_{Pr} = 12 \times 10^{-28}$ S m$^2$/site, (e) is for the set of DP samples with $c_{Pr} = 3 \times 10^{-28}$ S m$^2$/site and (f) is for the set of BER samples with $c_{Pr} = 3 \times 10^{-28}$ S m$^2$/site. The pH of 6.7 is used to model for all samples.
All data is now sufficient to model the SPCC as a function of electrolyte concentration from eq. (3.4) in combination with input parameters given by [27] in Table 3.3. Fig. 4.4 shows the experimental and modeled results of the SPCC for sample INDO1. The modeled result is implemented for three values of pH ($pH = 6, 7$ and 8) with the zeta potential offset $\zeta_o = 0.045\text{V}$ and the proton surface conductance $c_{Prot} = 3 \times 10^{-28} \text{S m}^2/\text{site}$. Fig. 4.4 shows that the model of the SPCC against the electrolyte concentration is very sensitive to the pH of the fluid as expected in [27]. The model is not in good agreement with the experimental result in particular at a low concentration where the deviation of SPCC from experimental data increases.

The deviation between the modeled and experimental results could arise from the formula proposed to calculate the zeta potential in eqs. (4.2 - 4.4). According to the model, the zeta potential in magnitude would decrease drastically with increasing the electrolyte concentration as shown in Fig. 4.5 (the solid line). However, based on the three measured values of the SPCC for all samples in Table 4.2 at the high electrolyte concentrations of $10^{-2}$M, $2 \times 10^{-2}$M and $5 \times 10^{-2}$M, the zeta potential at those corresponding concentrations is calculated by using eq. (1.10) as shown in Fig. 4.5 (the dashed line) for sample BereaUS5, for example. It is worthwhile noting that the surface conductance is neglected when the electrolyte concentration is higher than $10^{-2}$M as mentioned in chapter 3. It is obvious that the measured zeta potential slightly decreases with increasing concentration and can be roughly considered constant over the studied range of the electrolyte concentration. Similarly, the zeta potentials are experimentally obtained for other samples.

We therefore assume the zeta potential to be constant over the electrolyte concentration and that is also inferred from the collected experimental data presented in [69]. The dependence of the SPCC on the electrolyte concentration for all samples with corresponding proton surface conductance is experimentally and theoretically shown in Fig. 4.6 in which Fig. 4.6(a) is for the INDO1 sample, Fig. 4.6(b) is for the EST sample, Fig.4.6(c) is for the BEN6 and BEN7 samples, Fig. 4.6(d) is for the set of BereaUS samples, Fig. 4.6(e) is for the set of DP samples and Fig. 4.6(f) is for the set of BER samples, respectively. To avoid the overlap of the experimental data shown in Fig. 4.6(d) and Fig. 4.6(e), we only show the experimental graphs for four out of six samples for the sets of BereaUS and DP samples, respectively. All theoretical results are carried out for pH of 6.7 because this value is the average of measured values (between 6 and 7.5). For reasons of clarity, the SPCC is plotted against the reverse of the electrolyte concentration.
rather than the electrolyte concentration as shown in Fig. 4.6. This is because we want to avoid the experimental data locating just on the bottom left corner of the graphs at low electrolyte concentrations.

Fig. 4.6 shows that when the zeta potential is kept constant over the electrolyte concentration, the model is well capable of producing the main features of the experimental data. It is also seen that the SPCC is linearly proportional to the inverse of electrolyte concentration as expected at high concentrations when the surface conductance is ignored. This observation leads to the suggestion that the formula for the calculation of the zeta potential needs to be revised especially at a low concentration.

Due to the limitation of the model developed by Glover et al. \[27\] at low electrolyte concentrations, we have looked at other models to predict the streaming potential as a function of electrolyte concentration. For example, by fitting experimental data for quartz and NaCl or KCl at pH = 7 and T = 25°C, Pride and Morgan \[66\] obtain the relation

\[ \zeta = 8 + 26\log_{10}(C_f), \quad (4.9) \]

where \( \zeta \) is the zeta potential in mV and \( C_f \) is the electrolyte concentration in \( \text{mol/L} \).

Similarly, Vinogradov et al. \[67\] obtain the relation between the zeta potential and the electrolyte concentration based on published zeta potential data for quartz, silica and glass in NaCl at pH = 6-8 as below

\[ \zeta = -9.67 + 19.02\log_{10}(C_f), \quad (4.10) \]
By fitting experimental data collected for sandstone, sand, silica nanochannels, Stainton, and Fountainbleau with electrolytes of NaCl and KCl at pH = 6-8, Jaafar et al. [68] obtain an empirical expression between the SPCC and the electrolyte concentration

$$C_S = -1.36C_f^{-0.9123}, \quad (4.11)$$

where $C_S$ is expressed in mV MPa$^{-1}$.

Jouniaux and Ishido [69] obtain the other relation to predict the SPCC from fluid conductivity based on numerous measurements of the streaming potential on sand with NaCl at pH = 7-8 which have been published

$$C_S = \frac{-1.2 \times 10^{-8}}{\sigma_f}, \quad (4.12)$$

where $\sigma_f$ is the fluid electrical conductivity and $C_S$ is in V Pa$^{-1}$.

Putting eq. (4.9) and eq. (4.10) into eq. (3.4), the SPCC as a function of electrolyte concentration ($C_S-C_f$) is obtained for the models of Pride and Morgan and Vinogradov et al., respectively. From eq. (4.11), $C_S-C_f$ is directly obtained for model of Jaafar et al. To plot $C_S-C_f$ for the model of Jouniaux and Ishido from eq. (4.12), the fluid electrical conductivity as a function of electrolyte concentration obtained by fitting experimental data as shown in Fig. 4.3 is used. The prediction of the SPCC as a function of electrolyte concentration from all four empirical models is shown in Fig. 4.7.

Because all empirical models are mostly obtained for the silica based samples, experimental data for Bentheim sandstone mainly made up by silica (see Table 4.1) is used for the comparison as shown in Fig. 4.7. The prediction from the model of Glover et al. with the adjustment of the constant zeta potential for Bentheim sandstone shown Fig.4.6(c) is also repeated in Fig. 4.7. The comparison shows that the SPCC from all models converges and agrees with the experimental data at high electrolyte concentrations. However, at low concentrations (smaller than $10^{-2}$ M) the SPCC diverges from each other and does not agree with experimental data. Theoretical values from the models of Pride and Morgan as well as Vinogradov et al. are approximately twice as high as experimental values (see upper curves in Fig. 4.7). While theoretical values from the models of Jouniaux and Ishido and Jaafar et al. are approximately half of the experimental values (see lower curves in Fig. 4.7). Therefore, all four empirical models fail to predict the SPCC as
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Figure 4.8: (a) The streaming potential coupling coefficient versus time at room temperature for the sample BereaUS5 at an electrolyte concentration of $5 \times 10^{-3}$ M, (b) The relationship between viscosity and temperature.

The relationship between viscosity and temperature.

a function of electrolyte concentration even for the most used materials such as silica and NaCl at low electrolyte concentrations. Fig. 4.7 shows that the best approach to predict the SPCC as a function of electrolyte concentration is to use the modified model of Glover et al.

4.4.3 Streaming potential as a function of temperature

Before measuring the SPCC, we carry out a number of checks to be sure that the temperature dependence is measured accurately. That is because measurement of the SPCC as a function of temperature normally takes about 8h for each sample. During that time, the SPCC may change. To check how the SPCC varies over time, we measure the SPCC as a function of time at room temperature as shown in Fig. 4.8(a) by continuously pumping the fluid through the sample and measuring the SPCC after every a specific amount of time. Fig. 4.8(a) shows that initially the SPCC decreases drastically over time which could be due to the change of conductivity and pH (CO$_2$ uptake or electrode polarization drift or mineral decay from samples) and after about 40h, the SPCC gets relatively stable. Therefore, the SPCC as a function of temperature is picked after 40h.

To check how long it takes to get thermal equilibrium for the sample inside the core holder. We fix a sensor probe tip of the digital temperature meter (Omega DP460) on the sample outlet surface and find that the time period to get thermal equilibrium is around 45 minutes (temperature read out by the digital meter becomes the same as that read by the water bath when continuously pumping liquid
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Figure 4.9: Measured and modeled coupling coefficient as a function of temperature at $5 \times 10^{-3} \text{M}$ for sample IND01. Three $pH$ values (6, 7 and 8), three corresponding zeta potential offsets ($\zeta_o = 0.045 \text{V}, 0.083 \text{V}$ and 0.12V) and proton surface conductance $c_{\text{Prot}} = 3 \times 10^{-28} \text{S m}^2/$site are used to model.

We also measure viscosity of the liquid as a function of temperature as shown in Fig. 4.8(b) by comparing the slopes of flow rate-pressure difference straight lines (see [53]) at different temperatures to the reference slope at room temperature at which the fluid viscosity is known to be $0.96 \times 10^{-3} \text{Pa.s}$ [70]. Fig. 4.8(b) shows that the measured viscosities are in good agreement with eq. (4.6) suggested by [70]. To minimize the change of fluid electrical conductivity over time, we use a solution of the relatively high concentration of $5 \times 10^{-3} \text{M}$.

To model the SPCC as a function of temperature, the same argument as described in subsection 4.4.2 is used. The relative permittivity, the viscosity, the surface conductance, the disassociation constant and the fluid electrical conductivity at the concentration of $5 \times 10^{-3} \text{M}$ as a function of temperature are theoretically given in [27]. The zeta potential offset $\zeta_o$ is found by fitting the experimental data of the SPCC for each sample. Fig. 4.9 shows the experimental results and modeled results of the SPCC for sample IND01 in which three $pH$ values (6, 7 and 8), three corresponding zeta potential offsets ($\zeta_o = 0.045 \text{V}, 0.083 \text{V}$ and 0.12V) and proton surface conductance $c_{\text{Prot}} = 3 \times 10^{-28} \text{S m}^2/$site are used to model. It is seen that the SPCC versus temperature is also very sensitive to fluid $pH$ and $pH=6$ gives better fit than the others. Hence, $pH=6$ is used to model the SPCC as a function of temperature for the representative samples of EST, BereaUS5, DP217 and BER502 as shown in Fig. 4.10. Both the experimental and theoretical results show that the SPCC increases with increasing temperature. However, Fig.
4.10 shows a essential deviation between the experimental data and the model. The origin of that deviation is still unclear. One of the reasons may be due to a temperature activated transport process happening around 300 K, which obviously can not be explained by the model and requires further exploration.

### 4.5 Conclusion

We have measured the SPCC for 20 consolidated samples with 7 different concentration NaCl solutions and 9 different temperatures under well controlled conditions ($pH$, temperature, quality of distilled water). Afterwards the model is used by taking fluid parameters, rock-fluid interface parameters already provided in [27] and rock microstructure parameters (porosity, permeability and formation factor) measured by ourself for all samples. The comparisons are carried out for each sample.
For the concentration dependence of the SPCC, the comparison shows that the theoretical model is not in agreement with the experimental data, especially in low concentration range. However, if the zeta potential is considered to be constant over a small range of electrolyte concentration the model fits the experimental data very well. It leads to the suggestion that the formula of the zeta potential against electrolyte concentration in the model needs to be recalculated and adjusted accordingly. In addition to the model given in [27], we also use other models to predict the streaming potential as a function of electrolyte concentration. But all applied models fail to fit the experimental data at low electrolyte concentration. Therefore, further revisions of those models need to be carried out for a better fit at low electrolyte concentration. Of all the models used for the comparison, the modified model of Glover et al. [27] with assuming of constant zeta potential that is experimentally measured is the best approach to predict the SPCC as a function of electrolyte concentration. The modified model will in particular be useful in situations where experiments are difficult to perform for a big range of electrolyte concentration.

For temperature dependence of the SPCC, we implement a zeta potential offset to the model which improve the fit to experimental data. The comparison shows that the theoretical model does not fit well experimental data but it can reproduce the main trend of the experimental data. The reason for that could be due to the variation of the input parameters over temperature because the streaming potential coupling coefficient is sensitive to changes of the input parameters that describe the rock/fluid interface, such as the surface site density ($\Gamma_s$), the binding constant ($K_{Me}$) and the disassociation constant ($K_{(-)}$) [27]. Therefore, more research about the change of the input parameters versus temperature needs to be carried out for a better explanation. A possible explanation of the deviation at around 300K could be a temperature activated transport process. The results also show that the model is very sensitive to the $pH$ of the fluid, especially for the streaming potential coupling coefficient as a function of temperature. So the fluid $pH$ needs to be carefully taken into account during measurements.