Electrokinetics in porous media
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Chapter 5

Zeta potential of porous rocks in contact with monovalent and divalent electrolyte aqueous solutions

5.1 Introduction

In chapter 2, chapter 3 and chapter 4, all streaming potential measurements of porous media are carried out for NaCl solution only. However, in reality most reservoir rocks are saturated or partially saturated by natural waters. Natural waters normally contain mineral substances in the dissolved state (in the form of ions, complex ions). The main cations contained in natural waters are Ca$^{2+}$, Na$^+$, Mg$^{2+}$ and K$^+$ (mostly monovalent and divalent cations) and the main anions are Cl$^-$, SO$_4^{2-}$, HCO$_3^-$ and CO$_3^{2-}$ [43]. Therefore, the study of how the streaming potential coupling coefficient (SPCC) changes for different types of electrolytes is very important in geophysical applications.

In electrolytes, cations normally called counterions for the systems of reservoir rocks and electrolyte aqueous solutions influence the zeta potential most by affecting the surface charge, by changing the thickness of the electric double layer and the exact location of the shear plane [78]. The effect of counterions on the zeta potential on glass microchannels has been studied with Li$^+$/Na$^+$/K$^+$/Ca$^{2+}$/Ba$^{2+}$[79], Al$^{3+}$/Na$^+$[80], K$^+$/Mg$^{2+}$[81], Ca$^{2+}$/Mg$^{2+}$[82] and La$^{3+}$/Na$^+$[83]. Those studies show that properties of counterions like ionic strength, ionic valence, ionic size
and type of ions (monovalent, divalent or trivalent ions) affect the zeta potential. The study of the zeta potential as a function of the electrolyte resistivity, pH, and ionic compositions has also been carried out by Lorne et al. [84] for crushed rocks. In this chapter, we study the dependence of types of electrolytes on the zeta potential systematically for real porous reservoir rocks which are more relevant in geophysical applications.

To do so, streaming potential measurements are carried out for 5 representative consolidated samples (Bentheim Sandstone, Berea sandstone, Estaillade limestone, Indiana Limestone and Artificial ceramic core) that are also used in chapter 4 with 11 different monovalent and divalent electrolyte aqueous solutions at the concentration of $10^{-3} \, \text{M}$. The electrolyte solutions used for the measurements are NaI, NaCl, Na$_2$SO$_4$, KI, KCl, KNO$_3$, CsCl, MgSO$_4$, MgCl$_2$, CaCl$_2$ and CaSO$_4$. The reason for using the concentration of $10^{-3} \, \text{M}$ for all electrolytes is because that concentration is a typical value normally found in water that is in contact with the hydrocarbon-bearing formation [85]. From the SPCC with knowledge of the electrical conductivity, viscosity and electrical permittivity of the fluid, the zeta potential is obtained. Afterwards, the experimental results are analyzed in combination with theoretical models.

For 1:1 electrolytes, a theoretical formula for the zeta potential that has been already described in chapter 4 is used. For 2:2 electrolytes, we develop a new model based on the same procedures mentioned in [25–27] for divalent electrolytes. It should be noted that the models may not predict exactly absolute values of the zeta potentials especially at low electrolyte concentration as shown in chapter 4 but they can explain quantitatively the change of the zeta potential against types of electrolytes and types of rock. For a given electrolyte, the difference in the zeta potential can be explained by the difference in the surface site density and the disassociation constant for different kinds of porous rocks (mineral compositions). For a given porous sample, the difference in the zeta potential can be explained by the difference in the binding constant of cations and in cation types of electrolytes (monovalent or divalent cations).

This chapter has four remaining sections. In the first we briefly describe theoretical models to calculate the zeta potential for both monovalent and divalent electrolytes. In the second we present the experimental measurements. The third section contains the experimental results, the comparison between the experimental and the theoretical results and the discussion. Conclusions are provided in the final section.
5.2 Theoretical background of the zeta potential

To calculate the zeta potential, one needs to know the Debye length ($\chi_d$) and the Stern potential ($\phi_d$) as mentioned in chapter 4 ($\zeta = \phi_d \exp(-\chi_c/\chi_d)$). It should be noted that the shear plane distance ($\chi_c$) is assumed to be constant for different types of electrolytes [27].

For 1:1 electrolytes, NaCl for example, the denominator of the formula of the Debye length mentioned in eq. (1.7) can be written as

$$\sum \rho_\infty e^2 z_i^2 = [Na^+]e^2 z_i^2 + [Cl^-]e^2 z_i^2 = 2[Na^+]e^2, \quad ([Na^+] = [Cl^-])$$

$$= 2000 C_f N e^2, \quad ([Na^+] \text{ is in ions/m}^3) \quad (5.1)$$

where $e$ is the elementary charge, $N$ is the Avogadro’s number, $[Na^+]$ and $[Cl^-]$ is the ionic concentrations of $Na^+$ and $Cl^-$ in the bulk, respectively and $C_f$ is electrolyte concentration in mol/L.

Similarly, we obtain the expression of $\sum \rho_\infty e^2 z_i^2$ for 1:2 and 2:1 electrolytes and 2:2 electrolytes. Putting $\sum \rho_\infty e^2 z_i^2$ into eq. (1.7), the Debye length is expanded for different types of electrolytes as below

$$\chi_d = \begin{cases} \sqrt{\frac{e_0 k_B T}{2000 N e C_f}}, & \text{For 1:1 electrolytes such as NaCl, KCl, NaI, KI, KNO}_3 \text{ and CsCl} \\ \sqrt{\frac{e_0 k_B T}{6000 N e C_f}}, & \text{For 1:2 and 2:1 electrolytes such as Na}_2\text{SO}_4, \text{ MgCl}_2 \text{ and CaCl}_2 \\ \sqrt{\frac{e_0 k_B T}{8000 N e C_f}}, & \text{For 2:2 electrolytes such as CaSO}_4 \text{ and MgSO}_4 \end{cases} \quad (5.2)$$

The Stern potential for different types of electrolytes is calculated as follows:

5.2.1 For 1:1 electrolytes

For 1:1 electrolytes, the Stern potential, $\phi_d$, has an analytical form (see chapter 4 for more details):

$$\phi_d = \frac{2 k_B T}{3 e} \ln \left( \frac{\sqrt{8 \times 10^3 e_0 k_B T N (10^{-pH} + K_{Me} C_f)}}{2 e \Gamma_s K_{(-)}} \left[ C_f + 10^{-pH} + 10^{pH - pK_w} \right] \right), \quad (5.3)$$
5.2.2 For 2:2 electrolytes

However, no theoretical model is available for 2:2 electrolytes. Following the same procedures outlined in [25–27] (see Appendix B) we obtain a closed expression:

\[ X^6 + \left( \frac{10^{-pH}}{C_f K_{Me}} + \frac{e \Gamma_0 S \sqrt{I}}{C_f \sqrt{b}} \right) X^4 + \frac{K_{(-)} K_{Me}}{C_f^2 K_{Me} \sqrt{b}} X^2 = 0, \]  

(5.4)

where \( b = 8 \times 10^3 \epsilon_0 \epsilon_r k_b T N \), \( I \) is the ionic strength defined in Appendix B and \( X = e^{-e \phi_d / k_b T} \). In principle, eq. (5.4) can be solved to get an analytical solution but the solution is very complicated. Therefore, eq. (5.4) has been numerically solved to find \( X \) and the Stern potential \( \phi_d \) from the numerical values of input parameters presented in Section 5.4. It should be noted that only real root of eq. (5.4) is used to calculate the Stern potential \( \phi_d \) (see Appendix for more detail).

From eq. (5.1) to eq. (5.4), \( k_b \) is the Boltzmann’s constant, \( T \) is temperature (in K), \( \epsilon_0 \) is the dielectric permittivity in vacuum, \( \epsilon_r \) is the relative permittivity, \( \rho_{sci} \) is the ionic concentration of ions \( i \) in the solution, \( e \) is the elementary charge, \( z_i \) is the valency of ions \( i \), \( N \) is the Avogadro’s number, \( pH \) is the pH of fluid, \( K_{Me} \) is the binding constant for cation adsorption, \( K_{(-)} \) is the dissociation constant for dehydrogenization of silanol surface sites, \( \Gamma_s \) is the surface site density and \( C_f \) is the electrolyte concentration (in mol/L) (for more details, see [25–27]).

5.2.3 For 1:2 or 2:1 electrolytes

Because the zeta potential strongly depends on the types of counterion as mentioned in section 5.1. Therefore, we use eq. (5.3) to calculate the zeta potential for 1:2 electrolytes containing monovalent counterions (cations) such as Na_2SO_4 and eq. (5.4) for 2:1 electrolytes containing divalent counterions such as MgCl_2 or CaCl_2.

5.3 Experiments

Streaming potential measurements have been performed on 5 consolidated samples (EST, IND01, BER502, BEN6 and DP215). The mineral compositions and microstructure parameters (porosity, solid density, permeability and formation factor) have been measured and mentioned in chapter 3 and chapter 4 (see Tables 3.1 and 4.1).
The experimental setup for the streaming potential measurement (at room temperature - 22°C) is shown in Fig. 3.1. The solutions used in the measurements are 11 monovalent and divalent electrolyte aqueous solutions (NaCl, KCl, NaI, Na₂SO₄, KNO₃, CaSO₄, CsCl, MgCl₂, MgSO₄, CaCl₂, and KI) at the concentration of 10⁻³ M. All procedures of the measurement are the same as mentioned in previous chapters.

5.4 Results and discussion

5.4.1 Streaming potential coupling coefficient versus electrolyte types and sample types

The way used to obtain the SPCC is the same as described in chapter 3 and chapter 4. The SPCC for different electrolytes and different rocks is shown in Table 5.1. Based on Table 5.1, the dependence of the SPCC on types of electrolyte for different samples is shown in Fig. 5.1. It shows that at a given sample, the absolute values of the SPCC (|Cₛ|) for monovalent electrolytes are higher than that for divalent electrolytes. At a given electrolyte, |Cₛ| is the highest for the sample BEN6 (mostly silica) and the smallest for the sample IND (mostly calcite). In other words, |Cₛ| of the sample BEN6 saturated by monovalent electrolytes is around 35 times as high as that of the sample IND saturated by divalent electrolytes. This means that the coupling between the fluid flow and the electric potential strongly depends on the mineral compositions of the rocks and types of electrolytes. Because the coupling coefficient of the conversion between seismic waves and electromagnetic waves is theoretically the product of a complicated expression of frequency and the SPCC [32], the system of Bentheim sandstone and NaCl or NaI is one of the best ones for experimentally studying seismolectric effects.

5.4.2 Zeta potential versus electrolyte types and sample types

Viscosity, relative permittivity of electrolyte aqueous solutions and the formation factor of the samples are already known (see Tables 3.1 and 4.1). The electrical conductivity of the fully saturated samples are deduced from the sample resistances measured by an impedance analyzer (Hioki IM3570) [65]. Therefore, the zeta potential for different electrolytes is obtained based on eq. 1.9 as reported in
Table 5.1: The SPCC (mV/bar) and the effective conductivity of the samples, $\sigma_{eff}$ (mS/m) for different electrolytes

<table>
<thead>
<tr>
<th>Salt</th>
<th>BEN6 $C_\text{S}$ $\sigma_{eff}$</th>
<th>EST $C_\text{S}$ $\sigma_{eff}$</th>
<th>IND01 $C_\text{S}$ $\sigma_{eff}$</th>
<th>BER502 $C_\text{S}$ $\sigma_{eff}$</th>
<th>DP215 $C_\text{S}$ $\sigma_{eff}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>-288 19.2</td>
<td>-78 16.5</td>
<td>-43 19.3</td>
<td>-69 24.6</td>
<td>-232 22.3</td>
</tr>
<tr>
<td>KCl</td>
<td>-237 18.4</td>
<td>-63 16.7</td>
<td>-36 21.5</td>
<td>-45 24.7</td>
<td>-192 20.5</td>
</tr>
<tr>
<td>NaI</td>
<td>-291 19.8</td>
<td>-89 17.5</td>
<td>-52 19.2</td>
<td>-79 23.7</td>
<td>-285 18.5</td>
</tr>
<tr>
<td>Na$_2$SO$_4$</td>
<td>-200 28.5</td>
<td>-51 21.7</td>
<td>-34 28.6</td>
<td>-60 28.9</td>
<td>-136 26.1</td>
</tr>
<tr>
<td>KNO$_3$</td>
<td>-230 20.5</td>
<td>-63 17.5</td>
<td>-34 21.6</td>
<td>-54 24.0</td>
<td>-20 17.7</td>
</tr>
<tr>
<td>CaSO$_4$</td>
<td>-60 27.7</td>
<td>-21 19.0</td>
<td>-10 26.0</td>
<td>-17 29.0</td>
<td>-65 24.2</td>
</tr>
<tr>
<td>CaCl</td>
<td>-213 20.1</td>
<td>-65 17.5</td>
<td>-32 21.8</td>
<td>-39 23.1</td>
<td>-19 16.6</td>
</tr>
<tr>
<td>MgCl$_2$</td>
<td>-62 28.9</td>
<td>-24 21.9</td>
<td>-4.4 29.5</td>
<td>-23 28.3</td>
<td>-65 25.8</td>
</tr>
<tr>
<td>MgSO$_4$</td>
<td>-70 28.7</td>
<td>-37 21.0</td>
<td>-11 27.1</td>
<td>-23 27.9</td>
<td>-80 24.1</td>
</tr>
<tr>
<td>CaCl$_2$</td>
<td>-57 32.5</td>
<td>-13 24.0</td>
<td>-4.3 30.5</td>
<td>-15 30.5</td>
<td>-60 27.2</td>
</tr>
<tr>
<td>KI</td>
<td>-230 21.8</td>
<td>-52 19.6</td>
<td>-32 22.3</td>
<td>-60 24.8</td>
<td>-21 18.8</td>
</tr>
</tbody>
</table>

Figure 5.1: The absolute value of the SPCC ($|C_S|$) as a function of electrolytes. Continuous shaded regions represent error bounds of the measurement.

Table 5.2: The dependence of the zeta potential on types of electrolytes is shown in Fig. 5.2 and Fig. 5.3. The results show that the absolute values of the zeta potential ($|\zeta|$) depend not only on the samples but also on types of electrolytes.

For a given electrolyte, the order of increasing of $|\zeta|$ for the samples goes from IND01, EST, BER502, DP215 and BEN6, respectively. This can be qualitatively explained by the difference in the surface site density, the binding constant and the disassociation constant for different kinds of porous rocks (mineral compositions).

For a given sample, the order of decreasing of $|\zeta|$ goes from NaI, NaCl, Na$_2$SO$_4$, KI, KCl, KNO$_3$, CsCl, MgSO$_4$, MgCl$_2$, CaCl$_2$ and CaSO$_4$, respectively. The results also show that (1) the zeta potential for monovalent are higher than that for divalent electrolytes, (2) the zeta potential of the rocks is mainly affected by cations of electrolytes (counterions), (3) anions have little effect on the zeta potential. The
### Table 5.2: Zeta potential (mV)

<table>
<thead>
<tr>
<th>Salts</th>
<th>Sample</th>
<th>BEN6</th>
<th>EST</th>
<th>IND01</th>
<th>BER502</th>
<th>DP215</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>-78.1</td>
<td>-18.1</td>
<td>-11.6</td>
<td>-23.9</td>
<td>-73.2</td>
<td></td>
</tr>
<tr>
<td>KCl</td>
<td>-65.9</td>
<td>-14.8</td>
<td>-10.9</td>
<td>-15.6</td>
<td>-55.5</td>
<td></td>
</tr>
<tr>
<td>NaI</td>
<td>-84.3</td>
<td>-21.5</td>
<td>-14.1</td>
<td>-26.5</td>
<td>-74.5</td>
<td></td>
</tr>
<tr>
<td>Na$_2$SO$_4$</td>
<td>-80.5</td>
<td>-15.6</td>
<td>-13.6</td>
<td>-24.4</td>
<td>-50.1</td>
<td></td>
</tr>
<tr>
<td>KNO$_3$</td>
<td>-66.7</td>
<td>-15.6</td>
<td>-10.5</td>
<td>-18.2</td>
<td>-50.8</td>
<td></td>
</tr>
<tr>
<td>CaSO$_4$</td>
<td>-23.3</td>
<td>-5.7</td>
<td>-4.0</td>
<td>-6.8</td>
<td>-22.6</td>
<td></td>
</tr>
<tr>
<td>CaCl$_2$</td>
<td>-61.4</td>
<td>-16.1</td>
<td>-9.7</td>
<td>-12.6</td>
<td>-44.5</td>
<td></td>
</tr>
<tr>
<td>MgCl$_2$</td>
<td>-25.8</td>
<td>-7.3</td>
<td>-1.8</td>
<td>-9.3</td>
<td>-23.3</td>
<td></td>
</tr>
<tr>
<td>MgSO$_4$</td>
<td>-28.2</td>
<td>-11.0</td>
<td>-4.2</td>
<td>-9.1</td>
<td>-27.2</td>
<td></td>
</tr>
<tr>
<td>CaCl$_2$</td>
<td>-26.3</td>
<td>-4.3</td>
<td>-1.9</td>
<td>-6.6</td>
<td>-23.0</td>
<td></td>
</tr>
<tr>
<td>KI</td>
<td>-70.7</td>
<td>-14.3</td>
<td>-10.2</td>
<td>-21.0</td>
<td>-56.7</td>
<td></td>
</tr>
</tbody>
</table>

**Figure 5.2:** The absolute value of the zeta potential as a function of electrolytes. Continuous shaded regions represent error bounds of the measurement.

**Figure 5.3:** The absolute value of the zeta potential as a function of electrolytes.
difference in the zeta potential for a given sample can be qualitatively explained by the difference in the binding constant of cations and in types of cations (monovalent or divalent cations). For example, for the same type of cations (monovalent cations), the binding constant of $K^+$ is larger than $Na^+$ [27]. Therefore, at the same concentration more cations of $K^+$ are absorbed on the negative solid surface than cations of $Na^+$. This makes the electric potential on the shear plane (the zeta potential) smaller in the electrolyte containing $K^+$ that that in the electrolyte containing $Na^+$.

To quantitatively explain the behaviors in Fig. 5.2 and Fig. 5.3, we use the theoretical formulas mentioned in Section 5.2 to calculate the zeta potential using the input parameters that are already available in literature. For the sample BEN6, the mineral composition is mainly silica (see Table 4.1). Thus, we use input parameters given in the work of Glover at al. [27] for silica. The value of the dissociation constant, $K_{(-)}$, for dehydrogenization of silanol surface sites is taken as $10^{-7.1}$. The shear plane distance, $\chi_\zeta$, is taken as $2.4 \times 10^{-10}$ m. The surface site density, $\Gamma_s$, is taken as $5 \times 10^{18}$ site/m$^2$. The dissociation constant of water, $K_w$, at 22°C is $9.22 \times 10^{-15}$. The fluid pH is 6.7. The binding constant for cation adsorption on silica varies according to which is the dominant cations in the electrolyte and it is not well known. For example, $K_{Me}(Li^+)=10^{-7.8}$ and $K_{Me}(Na^+)=10^{-7.1}$ for silica given by Dove Rimstidt [86], $K_{Me}(Li^+)=10^{-7.7}$, $K_{Me}(Na^+)=10^{-7.5}$ and $K_{Me}(Cs^+)=10^{-7.2}$ given by Kosmulski and Dahlsten [87], $K_{Me}(Na^+)=10^{-3.25}$ and $K_{Me}(K^+)=10^{-2.8}$ given by Revil et al. [26]. By fitting experimental data for the zeta potential as shown in Fig. 5.4 for the sample BEN6, the binding constants for cations are obtained as $K_{Me}(Na^+)=10^{-5.5}$, $K_{Me}(K^+)=10^{-4.3}$, $K_{Me}(Cs^+)=10^{-2.9}$, $K_{Me}(Mg^{2+})=10^{-5.2}$ and $K_{Me}(Ca^{2+})=10^{-5.0}$. The binding constants for $Na^+$, $K^+$ and $Cs^+$ are in very good agreement with those given by Scales et al. [88] ($K_{Me}(Na^+)=10^{-5.5}$, $K_{Me}(K^+)=10^{-3.2}$, $K_{Me}(Cs^+)=10^{-2.8}$). The binding constant of $Mg^{2+}$ is lower than that of $Ca^{2+}$ due to the stronger absorption of $Ca^{2+}$ as shown in [82].

For the sample DP215, because its mineral composition (mostly alumina and fused silica as shown in see Table 4.1) is not the same as that of the sample BEN6, the rock/fluid interface parameters of the sample DP215 will be different from the sample BEN6. However, based on the theoretical model mentioned in Section 5.2, it is seen that the surface site density affects the zeta potential much more than the dissociation constant and the binding constant. Therefore, we keep all input parameters the same as above for the sample BEN6 except the surface site density. By fitting the experimental data (see Fig. 5.5), the surface site density for sample
Chapter 5. Zeta potential of porous rocks in contact with monovalent and divalent electrolyte aqueous solutions

Figure 5.4: The absolute value of the zeta potential as a function of electrolytes for the sample BEN6. Continuous shaded regions represent error bounds of the measurement.

Figure 5.5: The absolute value of the zeta potential as a function of electrolytes for the sample DP215. Continuous shaded regions represent error bounds of the measurement.

DP215 is found to be $\Gamma_z = 2.5 \times 10^{18}$ site/m$^2$. That value is lower than that of the sample BEN6.

For the samples BER502, EST and IND01, it is hard to quantitatively explain the experimental data by the models. The reason is that the mineral composition of those samples is a mixture of several minerals. Therefore, all input parameters such as the surface site density, the disassociation constant and the binding constant or the shear plane distance are not known well enough to be applied in the models.

It should be noted that the theoretical predictions do not show the effect of anions on the zeta potential as shown Fig. 5.4 and Fig. 5.5 (for example, the zeta potential is the same for NaCl and NaI). However, the experimental data shows that anions have a little effect on the zeta potential. Criscenti and Sverjensky [89] also show that electrolyte anions play a role in metal cation adsorption on the solid surfaces in salt solutions. Therefore, they influence the zeta potential. It suggests that the models need to be improved to take into account the effect of electrolyte anions.
To predict how the zeta potential behaves against the electrolyte concentration and the fluid pH for 2:2 electrolytes, we solve eq. (5.4) numerically to find $X$. The silica based sample and the 2:2 electrolyte of MgSO$_4$, for example, are used for the prediction. Therefore, input parameters for eq. (5.4) are $K_{\text{Me}}=10^{-7.1}$, $\chi_c=2.4\times10^{-10}$ m, $\Gamma_s=5\times10^{18}$ site/m$^2$, and $K_{Me}=10^{-5.2}$ (for the adsorption of counterion Mg$^{2+}$ on the silica surface). From the solution $X$, the Stern potential $\varphi_d$ and therefore the zeta potential have been obtained as a function of electrolyte concentration (the solid line in Fig. 5.6) and pH (the solid line in Fig. 5.7).

Based on Eq. (4.4), Eq. (5.2) and Eq. (5.3), we also predict the change of the zeta potential against the electrolyte concentration and the fluid pH for 1:1 electrolytes. The same argument for 2:2 electrolytes is used for the silica based sample and the 1:1 electrolyte of KCl. Therefore, the same input parameters as above ($K_{\text{Me}}$, $\chi_c$, $\Gamma_s$) are used except $K_{Me}=10^{-3.3}$ (for the adsorption of counterion K$^+$ on the silica surface). The change of the zeta potential against electrolyte concentration and fluid pH for 1:1 electrolytes are shown in Fig. 5.6 (the dashed line) and Fig. 5.7 (the dashed line), respectively.

Fig. 5.6 and Fig. 5.7 show that the zeta potential as a function of electrolyte concentration and pH have the same behaviors for both 1:1 and 2:2 electrolytes. The zeta potential in magnitude decreases with increasing electrolyte concentration and with decreasing fluid pH for both types of electrolytes. The theoretical values of the zeta potential for 2:2 electrolytes are less dependent on the fluid pH than those for 1:1 electrolytes. The reason is that the absorption process of the divalent cations is much less sensitive to pH as stated in [82].
The dependence of the zeta potential on the binding constant for cation adsorption for 1:1 and 2:2 electrolytes is also shown in Fig. 5.8 at the same condition (the same values for the disassociation constant, the shear plane distance, the surface site density, temperature, pH=6.7 and electrolyte concentration $C_f = 10^{-3}$ M). It shows that the zeta potential decreases with increasing binding constant as expected and the zeta potential for 1:1 electrolytes is always higher than that for 2:2 electrolytes at the same binding constant. That prediction is consistent with experimental data as shown in Fig. 5.2 and Fig. 5.3. Therefore, the theoretical model we develop for 2:2 electrolyte can explain the experimental results well.
5.5 Conclusion

In this chapter a systematic study of the zeta potential inferred from streaming potential measurements with 5 different consolidated samples saturated by 11 monovalent and divalent electrolyte aqueous solutions (NaCl, KCl, NaI, Na$_2$SO$_4$, KNO$_3$, CaSO$_4$, CsCl, MgCl$_2$, MgSO$_4$, CaCl$_2$ and KI). The experimental results show that the SPCC and the zeta potential strongly depend on the mineral composition and types of electrolytes (mainly types of cation). The difference in the SPCC among the samples and electrolytes can reach about 35 times. The experimental results also show that the zeta potential for monovalent electrolytes is higher than that for divalent electrolytes. The reservoir rocks made of silica have the highest zeta potentials when saturated by the same types of electrolyte.

The experimental results are explained by the theoretical models that are related to the rock/fluid interface parameters such as the surface site density, the disassociation constant, the binding constant and the shear plane distance. For 1:1 electrolytes, a theoretical model for the zeta potential calculation that has been well described by Revil and Glover [25], Revil et al. [26] and Glover et al. [27] is used. For 2:2 electrolytes, we develop another model based on the same procedures mentioned in [25–27] for 1:1 electrolytes and this model is able to produce the same results as predicted by Datta et al. [82] for the silica surface and the divalent electrolytes of MgCl$_2$ or CaCl$_2$.

The comparison shows that the theoretical models can explain the main behavior of the zeta potential against types of electrolytes and types of samples. For a given electrolyte, the difference in the zeta potential can be explained by the difference in the surface site density, the disassociation constant for different kinds of porous rocks (mineral composition). For a given sample, the difference in the zeta potential can be explained by the difference in the binding constant of cations and in types of cations (monovalent or divalent cations).