Electrokinetics in porous media
Luong, D.T.

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

General rights
It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations
If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: http://uba.uva.nl/en/contact, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.
Chapter 2

Streaming potential and electroosmosis measurements to characterize porous materials

2.1 Introduction

The coupling coefficient of conversion between seismic wave and electromagnetic wave depends strongly on the fluid conductivity, porosity, permeability, formation factor, pore size, zeta potential of porous media and other properties of the rock formation [32]. Therefore, determining these parameters is very important in studying electrokinetics in general and to model seismoelectric and electroseismic conversions. Li et al. [47] used ac measurements of streaming potential and electroosmosis to determine the effective pore size and permeability of porous media. Paillat et al. [14] used image analysis to determine the number of pores per cross sectional area of porous samples (pore density). The pore density is especially important in processes of contaminant removal from low permeability porous media under a dc electric field [14] and in building electroosmosis micropumps [48].

However, the method used in [14] did not work for porous media with very small pores such as Bentonite clay soils or tight-gas sandstones (the pore radius is smaller than 1 μm) that are relevant for application in the oil and gas industry [49]. In oil exploration and production, the typical pore sizes in rocks is the necessary information for considering the location of oil and fluid flow through the rocks. The characteristics of porous media also determine differential gas pressures needed to overcome capillary resistance of tight-gas sandstones in gas production.
Chapter 2. Streaming potential and electroosmosis measurements to characterize porous materials

Alternative methods such as nuclear magnetic resonance (NMR) or magnetic resonance imaging (IRM) can also be used to determine characteristics of porous media such as the porosity and pore size distribution, the permeability and the water saturation [50]. But this technique is quite expensive and is not able to determine the zeta potential - one of the most important parameters in electrokinetic phenomena. In this chapter, we use dc measurements of streaming potential and electroosmosis in porous samples and other simple measurements to fully characterize porous media and determine parameters needed for the study of seismolectric and electroseismic conversions. The approach works in particular well for very small pore samples.

This chapter has three sections. Section 2.2 presents the investigated samples and the experimental methods. Section 2.3 contains the experimental results and discussion. Conclusions are provided in Section 2.4.

2.2 Experiment

To demonstrate that characterization of porous media can be done by obtaining parameters such as porosity, permeability, formation factor, pore size, the number of pores and zeta potential of porous media through electrokinetics, streaming potential and electroosmosis measurements have been performed on 7 unconsolidated samples. Six are packs of spherical monodisperse particle with different diameters of the particles (10 μm, 20 μm, 40 μm, 140 μm, 250 μm and 500 μm). The monodisperse particles are obtained from Microbeads AS company, and are composed of polystyrene polymers. Those samples are designated as TS10, TS20, TS40, TS140, TS250 and TS500, respectively. It should be noted that the sample designated TS10 corresponds to the one with 10 μm particles and the similar for other samples. Beside monodisperse particle samples, we also use an unconsolidated sample made up of blasting sand particles obtained from Unicorn ICS BV company with diameter in the range of 200-300 μm (designated as $S_{\text{sand}}$).

Samples are constructed by filling polycarbonate plastic tubes (1 cm in inner diameter and 7.5 cm in length) successively with 2 cm thick layers of particles that are gently tamped down and shake by a shaker (TIRA-TV52110). Filter paper is used in both ends of the tube to retain the particles and is permeable enough to let the fluid pass through. The samples are then flushed with deionized water to remove any powder or dust.
Chapter 2. Streaming potential and electroosmosis measurements to characterize porous materials

We use a $10^{-3}$M NaCl solution of low enough conductivity of $10 \times 10^{-3}$ S/m measured by the conductivity meter (Consort C861) for the measurements. All measurements are carried out at room temperature ($22 \pm 1^\circ$C). When using low electrical conductivity solutions such as deionized water, the magnitude of the streaming potential coupling coefficient (SPCC) is large. However, the electrical conductivity of the saturated samples slowly stabilizes in about 24h for our samples. Perhaps due to CO$_2$ uptake from the air, that changes the conductivity.

2.2.1 Porosity, permeability, formation factor measurements

The way to measure the porosity, permeability of porous samples are the same as described in Appendix A for consolidated samples. Method of determining the tortuosity was proposed by Brown [51]. The formation factor $F$ is defined as:

$$F = \frac{\alpha_\infty}{\phi} = \frac{\sigma_f}{\sigma_S}$$

(2.1)

where $\alpha_\infty$ is the tortuosity, $\phi$ is the porosity of the sample, $\sigma_f$ is the fluid conductivity and $\sigma_S$ is the electrical conductivity of the fluid saturated sample. It should be noted that Eq. 2.1 is valid when surface conductivity effects become negligible (at high fluid conductivities, $\sigma_f$). For unconsolidated samples, we use the experimental setup similar to the one described in [52] and is shown in Fig. 2.1. The electrodes, Ag/AgCl mesh disks, are placed on both sides against the porous sample that is saturated successively with a set of aqueous NaCl solutions with different conductivities (0.13, 0.47, 0.81, 1.23, 1.51 and 1.98 S/m). The conductivities of those solutions are much higher than surface conductivity of the material, so the surface conductivity is negligible (for more detail, see [53]). The electrical conductivity is deduced from the resistance measurement using a Hioki IM3570 impedance analyzer at different frequencies (varying from 100Hz to 100 kHz).
2.2.2 Streaming potential measurement

The experimental setup for the measurement of the streaming potential is shown in Fig. 2.2. The pressure differences across the sample are created by a high pressure pump (LabHut, Series III- Pump) and measured by a pressure transducer (Endress and Hauser Deltabar S PMD75). The electrical potential is measured by two Ag/AgCl wire electrodes (A-M systems). The electrodes are put in the vicinity of the end faces of the sample but not within the liquid circulation to avoid the electrical noise from liquid movement around the electrodes [36]. The electrolyte from the outlet tube is not in contact with electrolyte used to pump liquid through the samples, preventing an electric current leakage through the liquid in the tube. The solution is circulated through the samples until the electrical conductivity and pH of the solution reach a stable value. Electrical potentials across the samples are then measured by a high input impedance multimeter (Agilent 34401A) connected to a computer and controlled by a Labview program (National Instruments). The electrical potentials at a given pressure difference fluctuate around a specific value as shown in Fig. 2.5. The Labview program averages the value of electrical potentials. The pH of equilibrium solutions, measured with the pH meter (Consort C861), are in the range of 7.1 to 7.6 and the solutions are also used for electroosmosis measurements.

2.2.3 Electroosmosis measurement

The experimental setup for the electroosmosis measurement is shown in Fig. 1.7. The same solution which was used in the streaming potential measurement is also used for this measurement. The zeta potential is consequently the same for both
kinds of measurements. The electrodes used to apply a dc voltage across the samples are perforated Ag/AgCl electrodes (MedCaT). To measure the maximum height difference, $\Delta h_{\text{max}}$, and the height difference as a function of time at a given voltage, cameras (Philips SPC 900NC PC) with the assistance of HandiAVI software are used to take pictures of the heights of the liquid columns over time. For each new measurement (new applied voltage, new sample) the samples are dried, mounted in the setup, evacuated by a vacuum pump and fully saturated by the same solutions.

It should be noted that when an applied voltage exceeds a critical value (1.48V for water [54]), there will be electrolysis at the anode and the cathode. These electrode reactions produce ions and gas in both electrodes. If these ions are not removed, these reactions induce a low in pH at the anode and a high pH at the cathode and a change in electrical conductivity. The rate of electrolysis reaction is largely determined by the current. If the current density is smaller than $<35 \mu$A per cm$^2$ cross sectional area, the effects due to the electrolysis can be ignored [55]. The resistances of the fully saturated samples that we use in this chapter are about 400 kΩ, so applied voltages are limited below 10V to avoid unwanted electrolysis effects.

2.3 Results and discussion

2.3.1 Porosity, permeability, formation factor

The measured porosity of the packs is 0.39 independently of the size of the particles with an error of 5%. Fig. 2.3 shows the typical graph of flow rate as a function of applied pressure difference for sample TS10.
Chapter 2. Streaming potential and electroosmosis measurements to characterize porous materials

Table 2.1: Measured properties of the samples. In which \( d \), \( k_o \), \( F \) and \( \sigma_S \) are diameter, permeability, formation factor and electrical conductivity of the saturated samples at equilibrium for all samples, respectively.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( d ) (in ( \mu )m)</th>
<th>( k_o ) (in ( m^2 ))</th>
<th>( F )</th>
<th>( \sigma_S ) (in S/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TS10</td>
<td>10</td>
<td>0.15 ( \times 10^{-12} )</td>
<td>4.0</td>
<td>4.1 ( \times 10^{-3} )</td>
</tr>
<tr>
<td>TS20</td>
<td>20</td>
<td>0.30 ( \times 10^{-12} )</td>
<td>4.2</td>
<td>3.6 ( \times 10^{-3} )</td>
</tr>
<tr>
<td>TS40</td>
<td>40</td>
<td>0.85 ( \times 10^{-12} )</td>
<td>4.2</td>
<td>3.0 ( \times 10^{-3} )</td>
</tr>
<tr>
<td>TS140</td>
<td>140</td>
<td>1.36 ( \times 10^{-12} )</td>
<td>4.3</td>
<td>3.1 ( \times 10^{-3} )</td>
</tr>
<tr>
<td>TS250</td>
<td>250</td>
<td>1.71 ( \times 10^{-12} )</td>
<td>4.0</td>
<td>3.5 ( \times 10^{-3} )</td>
</tr>
<tr>
<td>TS500</td>
<td>500</td>
<td>2.36 ( \times 10^{-12} )</td>
<td>4.3</td>
<td>2.9 ( \times 10^{-3} )</td>
</tr>
<tr>
<td>Sand</td>
<td>200-300</td>
<td>1.22 ( \times 10^{-12} )</td>
<td>4.0</td>
<td>3.0 ( \times 10^{-3} )</td>
</tr>
</tbody>
</table>

Figure 2.4: Saturated sample conductivity versus electrolyte conductivity for 2 samples (red dots for TS10 and blue cross symbols for TS500). The slopes of the straight lines yield the formation factors.

The graph shows that there is a linear relationship between flow rate and pressure difference and Darcy’s law is obeyed. So the flow is laminar and Eq. (1.8) and Eq. (1.9) are valid. This behavior is identical for all samples. Two measurements are performed for all samples to find the graphs of flow rate versus pressure difference. From the slope of the graph and Darcy’s law (the viscosity of the fluid is taken as \( 10^{-3} \) Pa.s), the permeability of the sample is calculated. We obtain permeabilities of all samples (see Table 2.1) with an uncertainty of 15% of the reported values.

An example of the electrical conductivity of the saturated samples versus the electrical conductivity of the electrolyte is shown in Fig. 2.4 for the 2 samples with the largest differences in the formation factors. We calculate the formation factor \( F \) as the reciprocal of the slope of a linear regression through the data points. Values of the formation factors for all samples are also reported in Table 2.1 with an error of 5%.

The measured formation factor of the samples is the range of 4.0 to 4.3 (see Table
2.1. According to Archie’s law [56], \( F = \phi^{-m} \) (\( F \) is the formation factor, \( \phi \) is the porosity of the sample and \( m \) is the so-called cementation exponent). \( m \) is found to be in the range 1.47-1.55. For unconsolidated samples made of perfect spheres, the exponent \( m \) should be 1.5 [57]. So the measured formation factors of the samples are in good agreement with Archie’s law. The electrical conductivities of the samples saturated by the solutions are also shown in Table 2.1.

2.3.2 Streaming Potential

The typical fluctuation of electrical potentials at a given pressure difference is shown in Fig. 2.5. The final value of electric potential for each pressure difference is taken as the average value of all data points.

The streaming potential as a function of pressure difference is measured twice for each sample. Fig. 2.6 shows two typical set of measurements for sample TS10 in which the second measurement is carried out 10h after the first one. The graph shows that there is a very small variation of streaming potentials with time (the drift is about 1 mV/h) and the straight lines fitting the data points do not go through the origin. This may be due to the electrode polarizations. However, this variation has no influence on the streaming potential coupling coefficient (SPCC) because the slopes of straight lines are almost the same for two separate measurements. The SPCC at 3 different electrical conductivities for sample TS10 is shown in Fig. 2.7. From Fig. 2.6 and Fig. 2.7, we see that the magnitude of the streaming potential is proportional to the driving pressure difference and inversely proportional to the liquid electrical conductivity, as expected from Eq. (1.8) and Eq. (1.9).
Chapter 2. Streaming potential and electroosmosis measurements to characterize porous materials

2.3.3 Electroosmosis

Fig. 2.8 shows the measured maximum height difference versus applied voltage for sample TS10. We observe that there is a linear relationship between the maximum height difference and the applied voltage as expected from Eq. (1.16) except the last data point (when the applied voltage is 7.5V). That last data point deviated from the linear trend could be due to the electrolysis happening on both electrodes as mentioned in section 3.4. Using the slope of the graph and the zeta potential...
Chapter 2. Streaming potential and electroosmosis measurements to characterize porous materials

Figure 2.8: Maximum height difference as a function of applied voltage for sample TS10.

Table 2.2: Calculated parameters of the samples. In which $\zeta$ is zeta potential in mV, $a$ is average pore radius in $\mu$m, $N$ is the number of pores per cross sectional area of the samples and $k_o$ is permeability of the samples in $m^2$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>TS10</th>
<th>TS20</th>
<th>TS40</th>
<th>TS140</th>
<th>TS250</th>
<th>TS500</th>
<th>$S_{surf}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\zeta$</td>
<td>-32.4</td>
<td>-5.2</td>
<td>-6.3</td>
<td>-12.5</td>
<td>-7.2</td>
<td>-9.1</td>
<td>13.7</td>
</tr>
<tr>
<td>$a$</td>
<td>2.3</td>
<td>3.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$N$</td>
<td>775$\times 10^4$</td>
<td>482$\times 10^4$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$k_o$</td>
<td>0.16$\times 10^{-12}$</td>
<td>0.31$\times 10^{-12}$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$a$ from [58]</td>
<td>1.5</td>
<td>2.9</td>
<td>5.9</td>
<td>20.6</td>
<td>36.8</td>
<td>73.5</td>
<td>-</td>
</tr>
</tbody>
</table>

obtained from streaming potential measurement, we can estimate the average pore size of the samples from eq. (1.16) as shown in Table 2.2.

Because of the limitation of applied voltage, the electroosmosis measurements are only performed for sample TS10 and TS20. The height difference as a function of time carried out for sample TS10 at possible maximum applied voltage of 6 V is shown in Fig. 2.9. The graph has an exponential curve as expected from Eq. (1.15). By using the exponential part of the graph, the response time in Eq. (1.13) is obtained (see Fig. 2.10). From the calculated response time and parameters of the samples, the number of pores on average can be determined by electroosmosis measurements (see Table 2.2).

To check the validity of the pore size estimation, we use the relationship between grain diameter and effective pore radius given by [58]

$$d = 2\theta a,$$

where $\theta$ is the theta transform function that depends on parameters of the porous
Chapter 2. Streaming potential and electroosmosis measurements to characterize porous materials

2.4 Conclusions

Streaming potential measurements have been performed for 7 unconsolidated samples fully saturated with a 10$^{-3}$M NaCl solution to determine the zeta potentials.
Because of the limitation of the voltage one can apply, we carry out the electroosmosis measurements for two smallest particle samples. This allows us to estimate average pore sizes of the samples as well as the number of pores per cross sectional area of porous media, which can not be determined by a method such as the image analysis performed in [14] for very small pore porous media. The estimated pore sizes and measured permeabilities have been compared to those calculated from the model of [58] to check the validity of the measurements.

The comparison shows that the measured pore sizes are in good agreement with the model of [58]. If the electroosmosis measurements can be improved e.g. by using ion-exchange membranes or a large cross sectional area of the samples to reduce the experimental time, this method can be effectively used to characterize porous media by using simple measurements, in particular for very small pore porous media that are relevant for application in the oil and gas industry.

Moreover, our measurements of streaming potential and electroosmosis also work for the interface between a liquid and a polymeric material. The polymer may be a more promising material for electroosmosis micropumps besides traditional materials like silica particles. The zeta potential of the polymer material that we use in this thesis is a little bit smaller than that of sands or sandstones.