



Original Article

Streaming Potential Coefficient Measurements in Porous Rocks Saturated by Divalent Electrolytes

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Abstract: Streaming potential in a water-rock system is generated by the relative motion between water and solid surfaces and is directly related to the existence of an electric double layer between water and solid grain surfaces of porous media. The streaming potential measurements have great potential in geophysical applications. Most porous rocks are filled by ground water containing various types of electrolytes. Therefore, it is important to understand the variation of the streaming potential with types of electrolytes for specific rocks. In this work, we have carried out streaming potential measurements for three consolidated rocks saturated by three divalent electrolytes at different electrolyte concentrations. The experimental result shows that the streaming potential coefficient in magnitude of all samples decreases with increasing electrolyte concentration. Additionally, an empirical relation between the streaming potential coefficient and the electrolyte concentration is obtained and it has a similar form to those available in literature for monovalent electrolytes.

Keywords: Streaming potential, zeta potential, porous materials, rocks, divalent electrolytes.

1. Introduction

Streaming potential plays an important role in geophysical applications because of its sensitivity to fluids inside porous materials. For example, the streaming potential measurements have been applied to detect subsurface flow patterns in oil reservoirs or in geothermal areas and volcanoes [1-3]. Monitoring of streaming potential anomalies has been proposed as a means of predicting earthquakes

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[4, 5] and detecting of seepage through water retention structures such as dams, dikes, reservoir floors, and canals [6]. An important parameter of streaming potential is the streaming potential coefficient because that controls the amount of coupling between the water flow and the electrical current in porous media. Porous rocks with different mineral compositions are filled or partially filled by ground water containing various types of electrolytes. Ground water commonly contains mineral substances in the dissolved state (in the form of ions, complex ions). Main cations in the ground water are Ca^{2+} , Na^+ , Mg^{2+} and K^+ (mostly monovalent and divalent cations), and main anions are Cl^- , SO_4^{2-} and CO_3^{2-} [e.g.,7]. Therefore, understanding the variation of the streaming potential coefficient with types of electrolytes and mineral compositions of rocks is crucial in geophysical applications. Although ground water contains mixtures of ionic species, it is sensible to study the streaming potential of porous rocks using a one-at-a-time approach. The dependence of the streaming potential coefficient on mineral compositions and types of monovalent electrolytes has been reported in literature for both porous rocks and sand packs [e.g., 8, 9]. Influence of divalent electrolytes on the streaming potential was also reported but at a single electrolyte concentration of 10^{-3} M [8].

In this work, we perform streaming potential measurements for consolidated rocks saturated by three divalent electrolytes at different electrolyte concentrations. From the measured streaming potential, we obtain an empirical relation between the streaming potential coefficient and the electrolyte concentration for divalent electrolytes that is not yet available in published work. It is seen that the obtained expression has a similar form to those reported in literature for monovalent electrolytes. The variation of the streaming potential coefficient with rocks can be qualitatively explained by the difference in mineral compositions.

2. Theoretical Background of Streaming Potential

Solid grains of porous rocks normally acquire a surface electric charge when brought into contact with electrolytes. The surface charge repels ions in the electrolyte whose charges have the same sign as the surface charge (called the "coions") and attracts ions whose charges have the opposite sign (called the "counterions" and normally cations) in the vicinity of the electrolyte-silica interface. This leads to the charge distribution known as the electric double layer (EDL). The EDL is made up of two layers: (1) the Stern layer, where cations are adsorbed on the surface and are immobile and (2) the diffuse layer, where the ions are mobile (see Fig. 1). In the bulk liquid, the number of cations and anions is equal so that it is electrically neutral. The closest plane to the solid surface in the diffuse layer at which flow occurs is termed the shear plane or the slipping plane, and the electrical potential at this plane is called the zeta potential (ζ) as shown in Fig. 1. The zeta potential depends on mineral composition of rocks and fluid properties [e.g., 9].

Due to the EDL, the electric current and the water flow are coupled in porous media. So the fluid flowing through porous media creates an electrical potential that is normally called streaming potential [11]. The streaming potential coefficient (SPC) at the steady state is defined as [8, 10 and references therein]:

$$C_s = \frac{\Delta V}{\Delta P} \quad (1)$$

where ΔV is the generated streaming potential and ΔP is the applied fluid pressure difference across a porous material. The SPC is a complicated function of electrical conductivity, pH, temperature of the

fluid, ionic species that are present in the fluid and mineral compositions of porous materials. From Eq. (1), the SPC can be experimentally determined by setting up a pressure difference ΔP across a porous sample and measuring the electric potential difference ΔV across it (see Fig. 2).

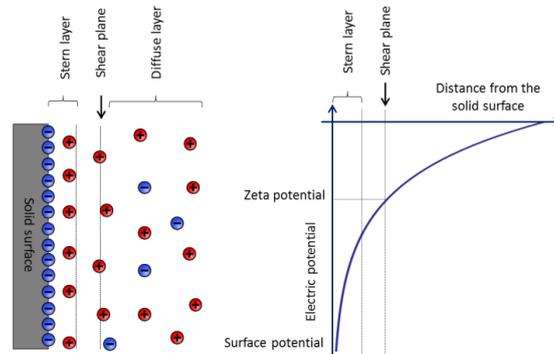


Figure 1. Stern model for the charge and electric potential distribution in the EDL at a solid-liquid interface.

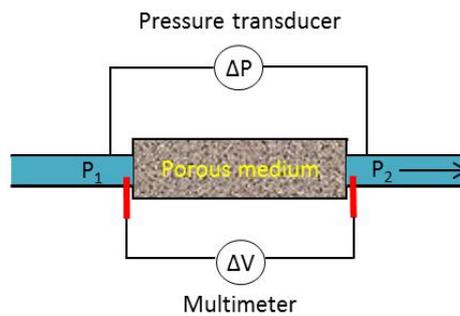


Figure 2. Schematic illustration of streaming potential measurement when the liquid is pumped through a porous sample. $\Delta V = V_{P1} - V_{P2}$ is a measured voltage and $\Delta P = P_{P1} - P_{P2}$ is the applied fluid pressure difference.

3. Experiment

Measurements are carried out for three rock samples with three divalent electrolytes (CaCl_2 , CaSO_4 and MgSO_4) at 5 different electrolyte concentrations (10^{-4} M, $5 \cdot 10^{-4}$ M, 10^{-3} M, $5 \cdot 10^{-3}$ M and 10^{-2} M). The rock samples are cylindrical cores (2.5 cm in diameter and 5.5 cm in length) of Bentheim sandstone (BEN), Berea sandstone and artificial ceramic sample. The mineral composition, permeability and porosity are shown in Table 1 [12]. All measurements are carried out at room temperature ($22 \pm 1^\circ\text{C}$).

Table 1. Mineral composition, permeability k_o (in mD) and porosity ϕ (in %) of the samples

#	Samples	Mineral compositions	k_o	ϕ
1	Bentheim sandstone	Mostly Silica	1382	22.3
2	Artificial ceramic	Fused silica and Alumina	430	44.1
3	Berea sandstone	Silica, Alumina, Ferric Oxide, Ferrous Oxide	310	20.1

The experimental setup for the measurement of the streaming potential is shown in Fig. 3. The core holder contains the porous samples. Each sample is surrounded by a thick silicone sleeve inside a conical stainless-steel cell and inserted into a stainless-steel holder to prevent flow along the interface of the sample. The electrolytes are circulated through the samples until the electrical conductivity and pH of the fluid reach a stable value. Electrical potential differences across the samples are measured by Ag/AgCl electrodes (A-M systems) using a high input impedance multimeter (Keithley Model 2700). The input resistance of the multimeter ($10\text{ G}\Omega$) is much larger than resistance of the saturated samples (around $200\text{ k}\Omega$) and therefore allows accurate measurements of electric potentials. Pressure differences across samples are measured by a high-precision differential pressure transducer (Endress and Hauser Deltabar S PMD75).

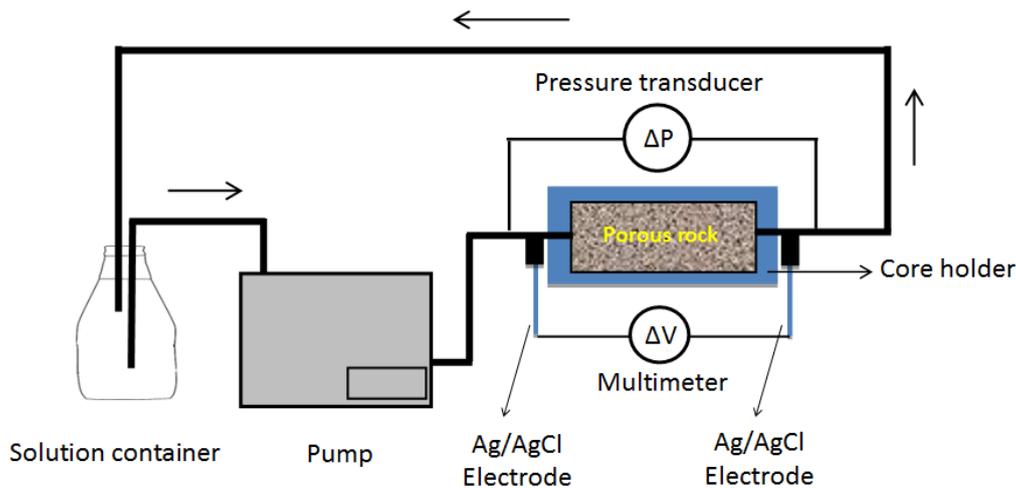


Figure 3. Schematic of the setup for streaming potential measurements.

4. Results and Discussion

The approach to obtain the SPC is similar to that has been well described in [e.g., 7, 10, 12] in which the streaming potential across the sample (ΔV) is measured as function of applied pressure difference (ΔP) at different flow rates controlled by the pump. Fig. 4 shows a representative example of the streaming potential as a function of pressure difference for the Bentheim sandstone at the 5.10^{-4} M CaCl_2 electrolyte. The SPC is then obtained as the slope of the straight line as indicated by Eq. (1). The average value of the SPC is obtained over three measurements. Table 2 shows the SPC for all samples saturated by different electrolytes at different electrolyte concentrations. It is shown that the SPC is always negative for all samples and all electrolytes and the negative sign of the SPC is suitable with published data in literature [e.g., 3, 7, 10, 12].

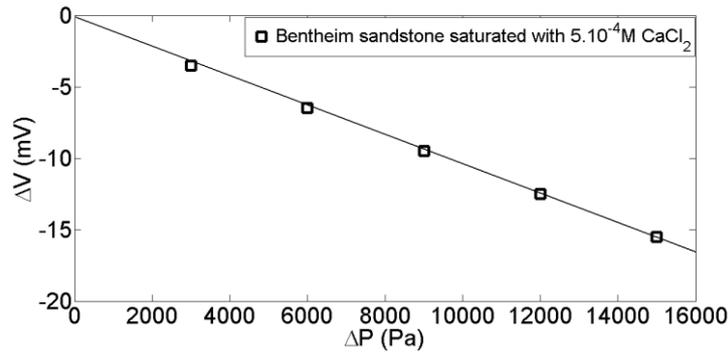


Figure 4. The ΔV - ΔP relation for Bentheim sandstone saturated by the 5.10^{-4} M CaCl_2 electrolyte.

Table 2. The SPC (mV/bar) for all samples and electrolytes at different electrolyte concentration.

Sample	Electrolyte	Concentration				
		10^{-4} M	5.10^{-4} M	10^{-3} M	5.10^{-3} M	10^{-2} M
Bentheim sandstone	CaCl_2	-330	-102	-61	-9.5	-4.5
	CaSO_4	-363	-110	-66	-22	-8.7
	MgSO_4	-343	-160	-92	-26	-13
Artificial ceramic	CaCl_2	-310	-95	-48	-9.0	-4.2
	CaSO_4	-297	-89	-48	-10.7	-5.6
	MgSO_4	-328	-129	-67	-19	-11
Berea sandstone	CaCl_2	-85	-37	-23	-6.7	-3.1
	CaSO_4	-81	-35	-24	-4.9	-3.5
	MgSO_4	-83	-45	-34	-12	-9.0

The experimental results show that the SPC strongly depends on rock types and electrolyte concentration. From the measured SPC in Table 2, the variation of magnitude of the SPC with rock types and electrolyte concentration for a representative electrolyte of MgSO_4 is shown in Fig. 5. The behavior in Fig. 5 is the same for two other electrolytes (CaCl_2 and CaSO_4). It is seen that the SPC in magnitude decreases with an increase of the electrolyte concentration for all studied rocks and that is in good agreement with published data in literature for monovalent electrolytes [e.g., 12-15].

Figure 6 shows the variation of the SPC in magnitude with rock types for all studied electrolytes at a representative concentration of 10^{-4} M. It is seen that the SPC of Bentheim sandstone and Artificial ceramic are almost the same but significantly higher than that of Berea sandstone (more than three times) at a given electrolyte concentration. This can be qualitatively explained by the mineral composition of rocks. Mineral composition of Bentheim sandstone and Artificial ceramic are quite similar (silica and alumina). Additionally, the binding constants of ions Ca^{2+} and Mg^{2+} are of same order of magnitude [e.g., 8]. Therefore, the SPC is almost the same for Bentheim sandstone and Artificial ceramic. However, it is seen that the presence of other minerals such as Ferric Oxide, Ferrous Oxide in rocks significantly reduces the SPC of Berea sandstone (for a detailed explanation by a theoretical model, see [8]).

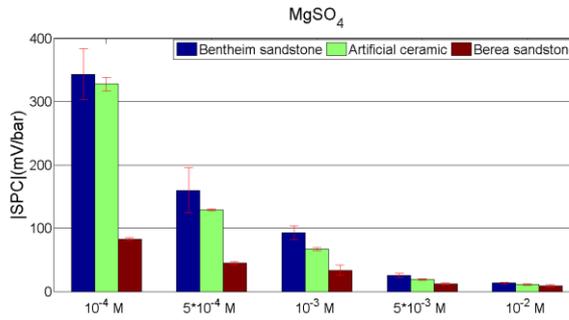


Figure 5. Variation of the SPC in magnitude with the electrolyte concentration for all rocks saturated by the MgSO₄ electrolyte.

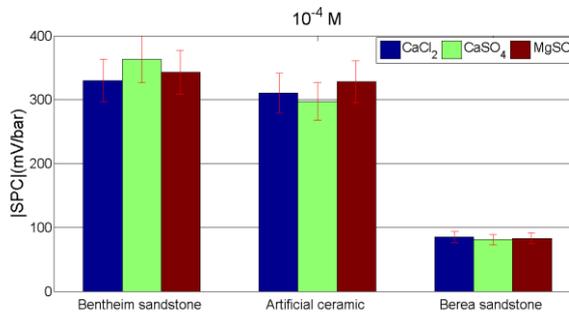


Figure 6. Variation of the SPC in magnitude with rock types for all studied electrolytes at 10⁻⁴ M concentration.

To obtain an empirical relation between the SPC and electrolyte concentration for silica-based rocks that are most commonly studied and reported in literature [e.g., 13, 14], the SPC in magnitude as a function of electrolyte concentration for Bentheim sandstone and Artificial ceramic saturated by all electrolytes is shown in Fig. 7. Based on the empirical dependence of the SPC (V/Pa) on the electrolyte concentration C_f (mol/L) reported in [13] for monovalent electrolytes, we fit the experimental data shown in Fig. 7 in the similar form and obtain the following SPC- C_f relation for divalent electrolytes:

$$C_s = 1.1 \times 10^{-9} C_f^{-0.91}. \tag{2}$$

It is noted that there are few empirical expressions in literature that can be used to estimate the SPC from the electrolyte concentration for monovalent electrolytes but there are not yet empirical expression relevant for divalent electrolytes. For example, Vinogradov et al. (2010) fitted experimental data for silica-based samples such as sandstone, sand, silica nanochannels, Stainton, and Fontainebleau but saturated by monovalent electrolytes of NaCl and KCl at pH = 6 - 8 and obtained an expression $C_s = 1.36 \times 10^{-9} / C_f^{0.9123}$ [13]. Additionally, one can deduce the expression $C_s = 1.2 \times 10^{-9} / C_f$ from [14] for monovalent electrolytes. Obviously, Eq. (2) has the similar form as those reported by [13, 14] but it is relevant for divalent electrolytes.

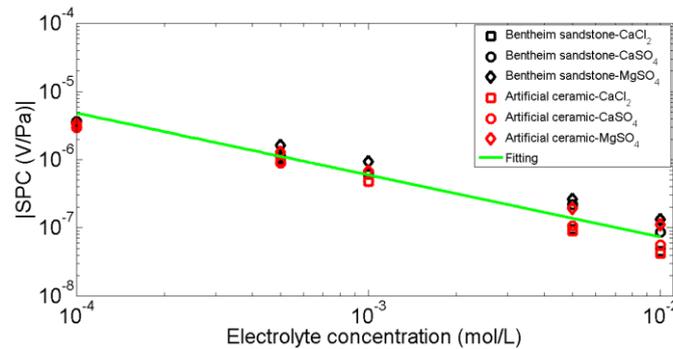


Figure 7. The SPC magnitude versus electrolyte concentration. Symbols are experimental data obtained in this work. Solid line is the fitting line.

5. Conclusions

The measurements of the SPC of three porous rocks saturated with three divalent electrolytes (CaCl_2 , CaSO_4 and MgSO_4) at five different electrolyte concentrations have been performed in this work. The experimental results show that the SPC in magnitude of all samples decreases with increasing electrolyte concentration for all electrolytes. It is also seen that the SPC of Bentheim sandstone and Artificial ceramic are almost the same but significantly higher than that of Berea sandstone at a given electrolyte concentration. That is due to the difference in mineral composition of rocks. From experimental data on the SPC, the empirical expression between the SPC and electrolyte concentration is obtained. The obtained expression has the similar form to those available in literature for monovalent electrolytes.

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