



RESEARCH ARTICLE

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Key Points:

- Measurements of TED and EED potentials in saturated sandstones, electrode effects
- Hittorf numbers are the same for TED and EED potentials
- SP in sandstones depend upon pore size, salinity, and rock texture in a complex way

Supporting Information:

- Readme
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Experimental measurements of the SP response to concentration and temperature gradients in sandstones with application to subsurface geophysical monitoring

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Abstract Exclusion-diffusion potentials arising from temperature gradients are widely neglected in self-potential (SP) surveys, despite the ubiquitous presence of temperature gradients in subsurface settings such as volcanoes and hot springs, geothermal fields, and oil reservoirs during production via water or steam injection. Likewise, with the exception of borehole SP logging, exclusion-diffusion potentials arising from concentration gradients are also neglected or, at best, it is assumed that the diffusion potential dominates. To better interpret these SP sources requires well-constrained measurements of the various coupling terms. We report measurements of thermoelectric and electrochemical exclusion-diffusion potentials across sandstones saturated with NaCl brine and find that electrode effects can dominate the measured voltage. After correcting for these, we find that Hittorf transport numbers are the same within experimental error regardless of whether ion transport occurs in response to temperature or concentration gradients over the range of NaCl concentration investigated that is typical of natural systems. Diffusion potentials dominate only if the pore throat radius is more than approximately 4000 times larger than the diffuse layer thickness. In fine-grained sandstones with small pore throat diameter, this condition is likely to be met only if the saturating brine is of relatively high salinity; thus, in many cases of interest to earth scientists, exclusion-diffusion potentials will comprise significant contributions from both ionic diffusion through, and ionic exclusion from, the pore space of the rock. However, in coarse-grained sandstones, or sandstones saturated with high-salinity brine, exclusion-diffusion potentials can be described using end-member models in which ionic exclusion is neglected. Exclusion-diffusion potentials in sandstones depend upon pore size and salinity in a complex way: they may be positive, negative, or zero depending upon sandstone rock texture (expressed here by the pore radius r) and salinity.

1. Introduction

Self-potential (SP) arising from concentration and temperature gradients across charged porous media are observed and measured in a number of scientific disciplines, including the earth, material, and environmental sciences [e.g., Marshall and Madden, 1959; Tasaka et al., 1965; Corwin and Hoover, 1979; Westermann-Clark and Christoforou, 1986; Revil, 1999; Kulesa et al., 2003; Darnet et al., 2004; Mainault et al., 2005; Linde and Revil, 2007; Martinez-Pagán et al., 2010; Gulamali et al., 2011]. The SP maintains overall electroneutrality when charge separation occurs in response to gradients in thermodynamic potential, such as electrochemical potential or fluid potential [e.g., Revil, 1999]. SP signals arise from diffusion (termed here diffusion potentials) when ions of contrasting mobility migrate at different rates down a concentration or temperature gradient in an electrolyte [e.g., Tasaka et al., 1965; Westermann-Clark and Christoforou, 1986; Revil, 1999]. SP signals arise from ion exclusion (termed here exclusion potentials) when there is a concentration or temperature gradient across a porous medium in which the solid surfaces are electrically charged. The surface charge gives rise to an electrical double layer in the adjacent electrolyte, which contains a deficit of co-ions of the same polarity as the surface charge, and an excess of counterions of opposing polarity [e.g., Revil et al., 1999]. If the thickness of the electrical double layer is significant relative to the pore size, there is exclusion of co-ions from the pore space, so a net excess of counterions migrates down the concentration or temperature gradient. This results in charge separation and establishes the exclusion potential [e.g., Tasaka et al., 1965; Westermann-Clark and Christoforou, 1986; Revil, 1999]. Here we use the terms electrochemical diffusion

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Table 1. Measured Values of Thermoelectric Exclusion-Diffusion Potentials Reported in the Literature^a

Reference	C _{TE} (mV/K)	Salinity (M)	Samples	Remarks
<i>Marshall and Madden</i> [1959]	0.23–0.48	Not reported	Sandstone, sandstone with clay, shale, limestone	KCl solutions. Values represent the difference in C _{TE} between rock samples and water.
<i>Nourbehect</i> [1963]	0.02–0.475 0.07–1.36 0.18–0.44 –0.09–1.12	Not reported	Sedimentary rocks Altered volcanics Quartz-lattice porphyry Dakota sandstone	Values represent the difference in C _{TE} between rock samples and water.
<i>Dorfman et al.</i> [1977]	0.49–1.35	Not reported	Variety of sandstones (Catahoula, Berea, Trenton, and Wall creek), serpentinite, and San Andreas limestone sandstone and shale	Values of C _{TE} of the rock samples and water. No account for electrode effect.
<i>Fitterman and Corwin</i> [1982]	0.01–0.18	0.372 and 0.372×10^{-2} NaCl, 0.054 KCl		Cerro-Prieto geothermal field cores
<i>Zlotnicki and Nishida</i> [2003]	–0.25–1.5 average of 0.2	Not reported	Not reported	Based on <i>Nourbehect</i> [1963] and <i>Dorfman et al.</i> [1977].
<i>Rosanne et al.</i> [2006]	0.71	0.006–0.08	Argillite	Coupled with salinity gradient.
<i>Revil et al.</i> [2013]	0.5	Deionized water; value not reported	Laboratory sandpack	First-order estimate based on observed SP and T anomalies.

^aAll measurements were obtained using NaCl electrolyte.

(also termed liquid junction) potential and electrochemical exclusion (also termed membrane) potential to describe the SP arising from concentration gradients; likewise, we use thermal diffusion (sometimes termed thermal junction) potential and thermal exclusion potential to describe the SP arising from temperature gradients. The SP arising from ion diffusion and exclusion is termed the exclusion-diffusion potential.

Measurements of SP arising from electrokinetic processes, observed when pressure gradients in the electrolyte cause counterions in the electrical double layer to move relative to the solid surfaces (also termed streaming potentials) [e.g., *Revil et al.*, 1999], have been used or proposed to characterize subsurface flow in numerous settings, including volcanoes [e.g., *Revil et al.*, 2003, 2008; *Ishido*, 2004; *Legaz et al.*, 2009; *Finizola et al.*, 2010; *Vandemeulebrouck et al.*, 2010], earthquake zones [e.g., *Mizutani et al.*, 1976; *Ishido and Mizutani*, 1981; *Jouniaux and Pozzi*, 1997], geothermal fields [e.g., *Fitterman and Corwin*, 1982; *Darnet et al.*, 2004; *Jardani et al.*, 2007, 2008; *Byrdina et al.*, 2009; *Jardani and Revil*, 2009], and hydrocarbon reservoirs [e.g., *Saunders et al.*, 2006, 2008, 2012], beneath glaciers [e.g., *Blake and Clarke*, 1999; *Kulesa et al.*, 2003], to detect leaks from dams, tanks, or embankments [e.g., *Ogilvy et al.*, 1969; *Martinez-Pagán et al.*, 2010; *Bolève et al.*, 2011; *Ikard et al.*, 2012] and to characterize groundwater flow and hydraulic properties [e.g., *Hunt and Worthington*, 2000; *Darnet et al.*, 2003; *Sailhac et al.*, 2004; *Rizzo et al.*, 2004; *Revil et al.*, 2005; *Jardani et al.*, 2006; *Maineult et al.*, 2008; *Jackson et al.*, 2012a, 2012b]. In many of these settings, exclusion-diffusion potentials may also make a significant contribution to the measured SP, because gradients in temperature and/or concentration are also present [e.g., *Corwin and Hoover*, 1979; *Fitterman and Corwin*, 1982; *Kulesa et al.*, 2003; *Darnet et al.*, 2004; *Maineult et al.*, 2005; *Martinez-Pagán et al.*, 2010; *Bolève et al.*, 2011; *Gulamali et al.*, 2011; *Revil et al.*, 2013]. However, despite their ubiquity in earth systems, few experimental measurements of exclusion-diffusion potentials arising from temperature or concentration gradients in natural porous media have been reported. This is in marked contrast to the numerous published experimental measurements of streaming potential, covering a wide range of natural samples of varying mineralogy and texture, saturated with electrolytes of varying composition and ionic strength [e.g., *Morgan et al.*, 1989; *Sprunt et al.*, 1994; *Jouniaux and Pozzi*, 1995, 1997; *Li et al.*, 1995; *Jiang et al.*, 1998; *Pangrea et al.*, 1999; *Reppert et al.*, 2001; *Guichet et al.*, 2003; *Reppert and Morgan*, 2003; *Revil et al.*, 2003, 2005; *Block and Haris*, 2006; *Jaafar et al.*, 2009; *Vinogradov et al.*, 2010; *Vinogradov and Jackson*, 2011; *Jackson and Vinogradov*, 2012].

Until recently, measurements of the exclusion-diffusion potential arising from temperature gradients in natural porous media had been almost entirely neglected; moreover, the few published studies typically provided only a limited description of the experimental conditions and methodology and failed to account for temperature-dependent electrode effects, which can significantly affect the measured potentials (see Table 1 for a summary). Only *Leinov et al.* [2010] provided a detailed description of an experimental methodology that explicitly accounts for electrode effects, and we show here an error in their reported data. More effort has been devoted to measuring the exclusion-diffusion potential arising from concentration gradients,

Table 2. Measured Values of Electrochemical Exclusion-Diffusion (Electrochemical) Potentials Reported in the Literature^a

Reference	Reported Potential (mV)	Concentration Ratio (C_1/C_2) (M)	Samples	Remarks
<i>Hill and Milburn</i> [1956]	−10.00–79.00 10.00–45.00 1.00–36.00	5.106/0.02–2.194	Clean sandstone Shaly sandstone Very shaly sandstone	Includes electrokinetic contribution. Concentration data were extracted from reported resistivity data.
<i>Nourbeht</i> [1963]	−8.27–13.00 −4.58–14.03 7.09–13.00	0.03/0.001	Sedimentary rocks Altered volcanics Quartz-latte porphyry	No description of the experimental procedure. Potential data were extracted from reported values in mV/decade.
<i>Ortiz et al.</i> [1973]	−3.54–68.09 −18.54–8.00	0.061/0.837	Sandstone (various grain sizes) Shaly and clean sandstones	Concentration data were extracted from reported resistivity data.
<i>Smits</i> [1968]	−47.10–−7.30	1.536/1.988–6.144	Shaly sandstone	Concentration data were extracted from reported molal concentration data.
<i>Thomas</i> [1976]	−75.00–−47.00	0.0955/1.198	Shaly sandstone	Concentration data were extracted from reported molal concentration data.

^aAll measurements were obtained using NaCl electrolyte.

motivated by the interpretation of borehole measurements of SP and electrical resistivity. Most of these studies appear in the petroleum literature, and their objective was to measure the cation exchange capacity (CEC) of shaly sandstones (i.e., sandstones containing significant quantities of clay minerals) [e.g., *Hill and Milburn*, 1956; *Smits*, 1968; *Ortiz et al.*, 1973; *Thomas*, 1976] (see Table 2 for a summary). These studies probed only a restricted range of sample mineralogy and NaCl electrolyte concentration; in some studies, the experimental methodology was not reported, and electrode effects may not have been accounted for or are included in the reported voltage measurements. More recently, *Revil et al.* [2005] reported measurements in argillaceous samples saturated with NaCl electrolyte, using an experimental method that accounts for electrode effects but was only briefly reported, while *Jougnot and Linde* [2013] addressed the importance of accounting for electrode effects in SP measurements. *Rosanne et al.* [2006] reported measurements of exclusion-diffusion potential across compacted clays, induced by simultaneous temperature and concentration gradients. Numerous studies have reported SP measurements from borehole logging tools, although interpretations are qualitative or only semiquantitative [e.g., *Doll*, 1949; *Hearst et al.*, 2000]. *Woodruff et al.* [2010] proposed a mechanistic model with a stochastic approach to invert SP borehole data for selected petrophysical properties that accounts for diffusion and streaming potentials.

The motivation and objectives for the present study are as follows. First, we wish to measure electrochemical and thermal exclusion-diffusion potentials (EED and TED, respectively) in sandstone samples that have little or no clay mineral content. As discussed above, published measurements of EED potentials have been acquired on shale or shaly sandstone samples, in which charge exclusion from the pore space is significantly affected by the presence of clay minerals. Yet the few published studies that include EED potentials when interpreting SP measurements neglect the effect of charge exclusion; diffusion potentials are assumed to dominate [*Kulesa et al.*, 2003; *Darnet et al.*, 2004; *Maineult et al.*, 2005; *Martinez-Pagán et al.*, 2010]. The first aim of this paper is, therefore, to determine whether it is reasonable to neglect exclusion potentials in sandstones for a range of rock texture and electrolyte concentration, when charge exclusion is not dominated by the presence of clay minerals.

Second, we wish to measure EED and TED potentials on the same (natural sandstone) samples, extending the measurements of TED potentials to the high-salinity domain typical of many saline aquifers and EED potentials to the low-salinity domain typical of freshwater systems. The few published measurements of TED are restricted the low-salinity domain, while EED measurements focus on the high-salinity domain. Moreover, it is generally assumed that ion transport and, specifically, the macroscopic Hittorf transport number (i.e., accounting for the presence of the electrically charged porous medium) are the same regardless of the driving thermodynamic potential [e.g., *Revil*, 1999]. We report the first well-constrained measurements of EED and TED potentials across the same natural samples, and the second aim of this paper is to determine whether the macroscopic Hittorf transport numbers are the same in both cases. TED potentials are widely neglected in SP surveys, despite the ubiquitous presence of temperature gradients in subsurface settings such as volcanoes and hot springs, geothermal fields, and oil reservoirs during production via water or steam injection [e.g., *Fitterman and Corwin*, 1982; *Darnet et al.*, 2004; *Jardani et al.*, 2007, 2008; *Byrdina et al.*, 2009;

Jardani and Revil, 2009; Revil et al., 2003, 2008; Ishido, 2004; Legaz et al., 2009; Finizola et al., 2010; Vandemeulebrouck et al., 2010; Gulamali et al., 2011]. If the Hittorf transport numbers are the same in both cases, it is possible to predict the contribution of TED potentials from EED potential measurements, and vice versa.

Third, we wish to determine the variation in exclusion-diffusion potential with rock texture and electrolyte concentration. Revil [1999] and Revil and Jougnot [2008] presented a model to predict the variation in macroscopic Hittorf number as a function of a parameter that represents the ratio of surface to bulk (electrolyte) electrical conductivity [Revil and Jougnot, 2008, equation (51)]. This parameter can be estimated from measurements of porosity, the CEC, the mobility of counterions along the mineral surfaces, and the electrolyte conductivity [Revil and Jougnot, 2008, equations (53) and (61)]. It is a proxy for the relative contribution of exclusion and diffusion potentials: when the parameter is large (corresponding to a large CEC, surface counterion mobility, and low bulk electrical conductivity), the exclusion potential dominates, and vice versa. However, measurements of the CEC and counterion mobility are often not available, especially in clean sandstones in which the CEC is assumed to be small. Moreover, it is well known that the relative contribution of diffusion and exclusion potentials to the EED or TED potential depends upon the mobility contrast between the co-ions and counterions, and the thickness of the electrical double layer relative to the pore radius [e.g., Ortiz et al., 1973; Westermann-Clark and Christoforou, 1986]. Westermann-Clark and Christoforou [1986] presented a simple model to predict the relative contribution of exclusion and diffusion potentials (the “exclusion efficiency”) as a function of the ratio of the pore throat radius to the thickness of the electrical double layer. The third aim of this paper is, therefore, to determine whether the exclusion efficiency can be predicted from measurements of pore size distribution and electrolyte concentration, which may allow simple and rapid estimation of thermoelectric and electrochemical potentials in natural porous media saturated with NaCl-dominated brines.

Fourth, we present an experimental methodology to measure exclusion-diffusion potentials that result from gradients in temperature or concentration across natural porous samples, which accounts for electrode effects. Such a methodology has not been reported previously and is an extension of the approach used by Leinov et al. [2010]. Finally, we discuss the implications of our findings for the interpretation of SP measurements in natural systems in which there are gradients in concentration and/or temperature, in addition to gradients in fluid pressure.

2. Theory

We consider charged porous media with heat and ion transport in a 1-1 electrolyte in the absence of viscous or body forces. Theoretical descriptions of the exclusion-diffusion potentials arising from temperature and concentration gradients have been provided by a number of authors [Marshall and Madden, 1959; Tasaka et al., 1965; Sen, 1989; Revil, 1999; Leinov et al., 2010], and we present only a brief summary here.

2.1. TED Potential

The gradient in electrical potential can be related to the gradient in temperature across a charged porous medium when no gradient in concentration is present and the total current density is zero, to yield [Leinov et al., 2010]

$$\nabla V_{\text{TED}} = -(2T_+ - 1)\nabla T \frac{k_B}{e} \ln a + \left[\frac{T_+}{e} \left(s_+^0 - \frac{Q_+^*}{T} \right) - \frac{T_-}{e} \left(s_-^0 - \frac{Q_-^*}{T} \right) \right] \nabla T \quad (1)$$

where k_B is Boltzmann’s constant, e is the charge of an electron, a is the activity of the electrolyte, $s_{\pm}^0$ are the partial molal entropies of the cations and anions at the reference level, $Q_{\pm}^*$ represent the cross coupling between the temperature gradient and the resulting salinity gradient and are defined as the heat transported by unit diffusion flux of cations and anions, T represents temperature, and $T_{\pm}$ are the macroscopic Hittorf transport numbers,

$$T_{\pm} = \frac{\sigma_{\pm}}{\sigma_+ + \sigma_-} \quad (2)$$

where $\sigma_{\pm}$ are the electrical conductivities of the cations and anions and

$$T_+ + T_- = 1 \quad (3)$$

If we assume that $Q_{\pm}^*$ varies linearly with temperature, so $Q_{\pm}^*/T$ is constant over the concentration and temperature ranges investigated in this study, then equation (1) can be integrated to yield

$$\Delta V_{\text{TED}} = -(2T_+ - 1)\Delta T \frac{k_B}{e} \ln a + \left[\frac{T_+}{e} \left(s_+^0 - \frac{Q_+^*}{T} \right) - \frac{T_-}{e} \left(s_-^0 - \frac{Q_-^*}{T} \right) \right] \Delta T \quad (4)$$

where ΔV_{TED} is the measured voltage difference across a charged porous medium.

The thermoelectric coupling coefficient is defined as the ratio of the thermoelectric potential to the temperature difference:

$$C_{\text{TED}} = \frac{\Delta V_{\text{TED}}}{\Delta T} = -(2T_+ - 1) \frac{k_B}{e} \ln a + \frac{T_+}{e} \left(s_+^0 - \frac{Q_+^*}{T} \right) - \frac{T_-}{e} \left(s_-^0 - \frac{Q_-^*}{T} \right) \quad (5)$$

Equation (5) is equivalent to equation (14) of *Tasaka et al.* [1965].

We can identify two end-member cases when thermal diffusion or exclusion potentials dominate. One end-member is that of a perfect membrane, where co-ions are entirely excluded from the pore space; if the solid surfaces are negatively charged, this corresponds to $T_+ = 1$ (and vice versa). The thermal exclusion potential for a negatively charged porous medium is therefore given by

$$\Delta V_{\text{TE}}|_{(T_+=1)} = -\frac{k_B \Delta T}{e} \ln a + \frac{\Delta T}{e} \left(s_+^0 - \frac{Q_+^*}{T} \right) \quad (6)$$

The other end-member is that of an uncharged porous media, where the gradient in thermoelectric potential is identical to that of the saturating electrolyte; thus, $T_{\pm} = t_{\pm}$, where t_+ and t_- are the microscopic Hittorf transport numbers of the cations and anions, given by

$$t_{\pm} = \beta_{\pm} / (\beta_+ + \beta_-) \quad (7)$$

where $\beta_{\pm}$ are the ionic mobilities and

$$t_+ + t_- = 1 \quad (8)$$

The thermal diffusion potential is therefore given by

$$\Delta V_{\text{TD}}|_{(T_+=t_+)} = -(2t_+ - 1)\Delta T \frac{k_B}{e} \ln a + \left[\frac{t_+}{e} \left(s_+^0 - \frac{Q_+^*}{T} \right) - \frac{t_-}{e} \left(s_-^0 - \frac{Q_-^*}{T} \right) \right] \Delta T \quad (9)$$

In NaCl electrolyte, $t_+ = t_{\text{Na}}$ (the ionic transport number of the Na ions) and can be described by [Gulamali et al., 2011]

$$t_{\text{Na}} = \begin{cases} 0.3962, C < 0.09 \text{ M} \\ 0.3655 - 9.2 \times 10^{-3} \ln(C), C \geq 0.09 \text{ M} \end{cases} \quad (10)$$

where C is the electrolyte concentration [e.g., *Braun and Weingartner*, 1985; *Panopoulos et al.*, 1986, and references therein]. The concentration of the electrolyte is related to its activity a via the activity coefficient γ [e.g., *Bockris and Reddy*, 1973; *Hamer and Wu*, 1972]

$$a = \gamma C \quad (11)$$

2.2. EED Potential

The gradient in electrochemical exclusion-diffusion potential can be related to the gradient in concentration (expressed here as activity a) across a charged porous medium when no gradient in temperature is present and the total current density is zero, to yield [Revil, 1999]

$$\nabla V_{\text{EED}} = -\frac{k_B T}{e} (2T_+ - 1) \nabla \ln a \quad (12)$$

Integrating equation (12) yields an expression for the electrochemical potential across a porous medium connecting two electrolyte reservoirs of contrasting activity a_1 and a_2

$$\Delta V_{\text{EED}} = -\frac{k_B T}{e} \int_{a_1}^{a_2} (2T_+ - 1) d \ln(a) \quad (13)$$

As before, we can identify the two end-member cases when chemical diffusion or exclusion potentials dominate. The end-member of a perfect membrane, with negatively charged solid surfaces, corresponds to $T_+ = 1$ and the chemical exclusion potential is given by

$$\Delta V_{EE}|_{(T_+=1)} = -\frac{k_B T}{e} \ln(a_2/a_1) \quad (14)$$

The end-member of an uncharged porous medium corresponds to $T_+ = t_+ = t_{Na}$ for a NaCl electrolyte, and the chemical diffusion potential formulation is identical to equation (13) with t_{Na} substituted instead T_+ .

However, equation (10) suggests that t_{Na} is only weakly dependent on concentration, varying by less than 15% over the concentration range 0.09 M to 3.7 M. Assuming t_{Na} is constant and independent of concentration, equation (13) can be simplified to yield the chemical diffusion potential

$$\Delta V_{ED}|_{(T_+=t_{Na})} = -\frac{k_B T}{e} (2t_{Na} - 1) \ln(a_2/a_1) \quad (15)$$

2.3. Electrode Effects in Laboratory Measurements of TED and EED Potentials

In our laboratory experiments (described in the next section) we measure the electrical potential across saturated sandstone samples connected to two reservoirs containing either NaCl electrolyte of uniform concentration C and contrasting temperature T_1 and T_2 or uniform temperature T and contrasting concentrations C_1 and C_2 . The apparent potential measured across the porous sample (ΔV_{AP}) includes the exclusion-diffusion potential (ΔV_{TED} or ΔV_{EED}) induced by the temperature or concentration gradient and also a temperature- or concentration-dependent electrode potential ΔV_C [Leinov *et al.*, 2010]

$$\Delta V_{AP} = \Delta V_{TED/EED} + \Delta V_C \quad (16)$$

We eliminate the electrode potential by measuring the apparent voltage along a column (described in the next section) containing NaCl electrolyte of the same concentration C and contrasting temperature (T_1 and T_2), or the same temperature T and contrasting concentrations (C_1 and C_2), using identical electrodes, but in the absence of the porous sample. The apparent voltage measured along the column (ΔV_{AC}) is given by the thermal or chemical diffusion potential ($\Delta V|_{T_+=t_{Na}}$) induced by the thermal or concentration gradient, and the electrode potential (ΔV_C)

$$\Delta V_{AC} = \Delta V|_{T_+=t_{Na}} + \Delta V_C \quad (17)$$

Combining equations (4), (9), (16), and (17) yields an expression for the thermal exclusion-diffusion potential for a sample saturated with NaCl electrolyte in which electrode effects are eliminated

$$\Delta V_{TED} = \Delta V_{AP} - \Delta V_{AC} - (2t_{Na} - 1) \frac{k_B(T_2 - T_1)}{e} \ln a + \frac{(T_1 - T_2)}{e} \left[t_{Na} \left(s_{Na}^0 - \frac{Q_{Na}^*}{T} \right) - t_{Na} \left(s_{Cl}^0 - \frac{Q_{Cl}^*}{T} \right) \right] \quad (18)$$

and combining equations (15)–(17) yields the equivalent expression for the electrochemical exclusion-diffusion potential

$$\Delta V_{EED} = \Delta V_{AP} - \Delta V_{AC} - \frac{k_B T}{e} (2t_{Na} - 1) \ln(a_2/a_1) \quad (19)$$

We describe the measurement of the apparent voltage across the porous sample (ΔV_{AP}) and column (ΔV_{AC}) in the next section.

3. Experimental Method

Electrical potentials induced by temperature or concentration gradients were measured using two types of experimental apparatus (Figure 1). The “plug” apparatus facilitates measurement of the voltage across a saturated rock sample in contact with reservoirs containing electrolyte of contrasting temperature or concentration (Figures 1a and 1c); the “column” apparatus facilitates measurement of the voltage across the electrolyte and allows us to account for temperature- and concentration-dependent electrode effects (Figures 1b and 1d). In all experiments, voltage measurements were obtained using nonpolarizing Ag|AgCl

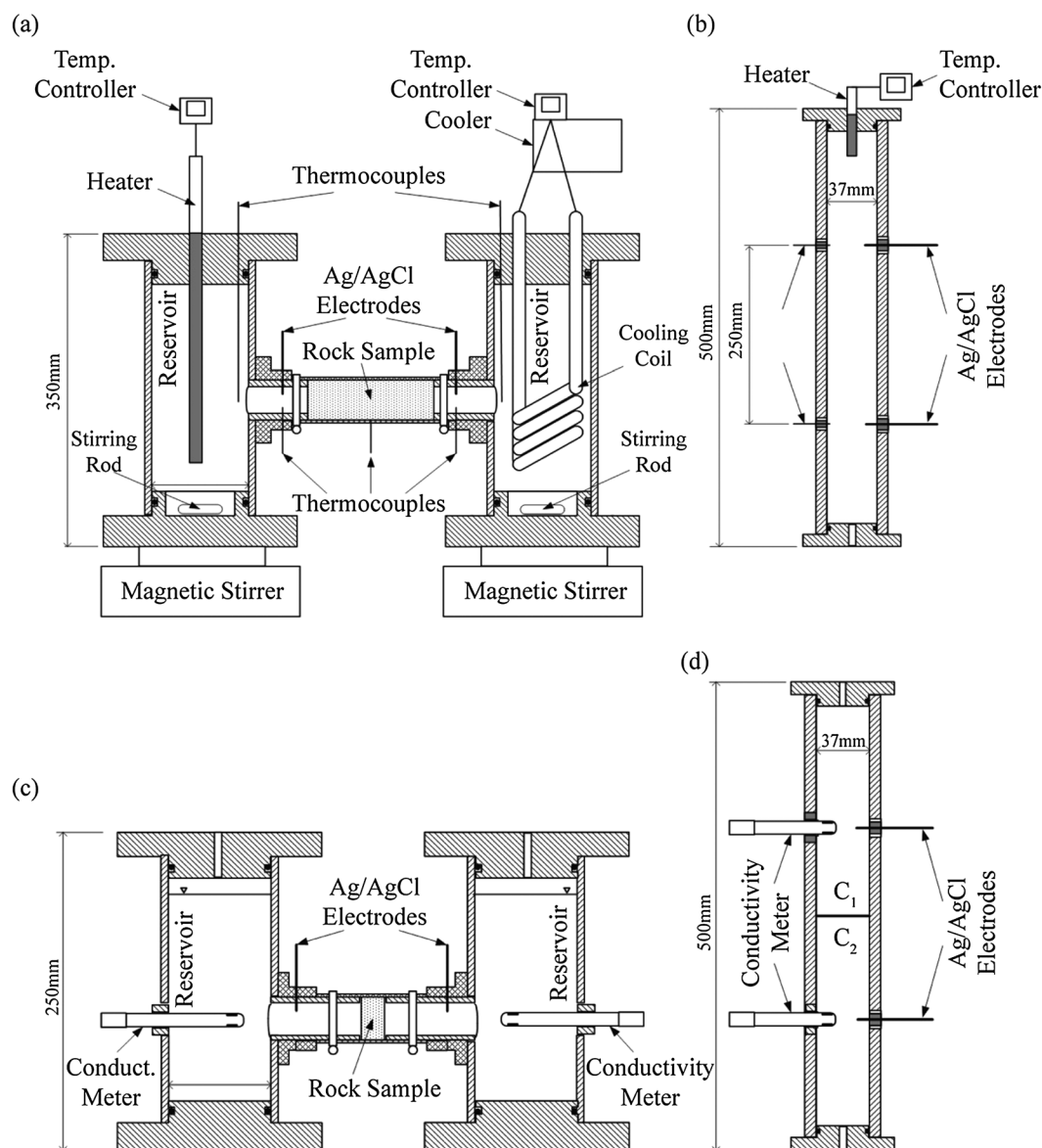


Figure 1. Apparatus for measuring (a, b) thermoelectric exclusion-diffusion potentials and (c, d) electrochemical exclusion-diffusion potentials. Setups in Figures 1a and 1c allow exclusion-diffusion potentials to be measured across rock samples (the “plug apparatus”); setups in Figures 1b and 1d allow exclusion-diffusion potentials to be measured across the electrolyte alone (the “column apparatus”). The latter measurements are used to eliminate electrode effects.

electrodes (noise levels $<100 \mu\text{V}$) and an NI-9219 voltmeter (internal impedance $>1 \text{ G}\Omega$, accuracy of 0.18% and resolution of 50 nV). The electrical conductivity of the electrolytes was measured using Jenway 4520 conductivity meters ($\pm 0.5\%$ accuracy, $0.01 \mu\text{S}/\text{cm}$ – $0.01 \text{ S}/\text{cm}$ resolution); the temperature of the electrolytes was measured using T-type isolated thermocouples (accuracy $\pm 0.5^\circ\text{C}$). Voltage, temperature, and conductivity values were recorded at a 0.1 Hz sampling frequency.

Measured conductivity values (σ in S m^{-1}) were converted into concentration values (C in M) following the approach of Vinogradov et al. [2010]. They related the conductivity of NaCl electrolyte to NaCl concentration using an empirical correlation [Worthington et al., 1990] and published data [Sen and Goode, 1992; Lide, 2009] at 23°C . A comparison between these sources showed good agreement at low electrolyte conductivity, but significant differences for conductivity $>1 \text{ S m}^{-1}$ [see Vinogradov et al., 2010, Figure 7]. They therefore combined the sources, using the expression of Worthington et al. [1990] for electrolyte conductivity $<1 \text{ S m}^{-1}$ and,

Table 3. Rock Samples Used in the Experimental Program

Experiment Type	Thermoelectric			Electrochemical
Sample Origin	Doddington	St. Bees #2	Stainton	Doddington
	Sandstone outcrop at Doddington, UK	Sandstone outcrop at St. Bees, UK	Sandstone outcrop at Stainton, UK	Sandstone outcrop at Doddington, UK
Dimensions (cm × cm)	7.7 × 3.7 diameter	7.7 × 3.7 diameter	7.58 × 3.6 diameter	1 × 3.7 diameter
Porosity (%)	18	19	13	18
Permeability (mdarcy)	850	30	2	850
Mean pore throat radius	12	5.3	6	12

at higher conductivity, a new polynomial function of the same order as that suggested by *Worthington et al.* [1990], fitted to published data in *Weast* [1989] and *Sen and Goode* [1992]

$$C = 5.9738 \times 10^{-7} \sigma^6 - 3.5136 \times 10^{-5} \sigma^5 + 7.823 \times 10^{-4} \sigma^4 - 8.0334 \times 10^{-3} \sigma^3 + 4.0791 \times 10^{-2} \sigma^2 + 3.4996 \times 10^{-2} \sigma + 3.6104 \times 10^{-2} \quad (20)$$

where concentration is in M and conductivity is in $S\ m^{-1}$.

Three different quartz-dominated sandstone core samples were used in the experiments (see Table 3). The Doddington sample is the same as that used by *Leinov et al.* [2010], the St. Bees #2 sample is the same as that used *Jaafar et al.* [2009] and the Stainton B sample is the same as that used by *Vinogradov and Jackson* [2011]. The electrolyte consists of solutions of NaCl in deionized water (the conductivity of the deionized water is $<5\ \mu S/cm$) over the concentration range 10^{-4} – $1\ M$.

3.1. Measurements of TED Potential

The “TED” plug apparatus to measure the thermal exclusion-diffusion potential consists of two reservoirs connected by a horizontal rubber sleeve which is used as the sample holder (Figure 1a). The sleeve fits tightly around the sample to ensure that ion transport can only occur through the sample. Both reservoirs and sleeve are thermally and electrically isolated. The reservoirs and sleeve are filled with NaCl electrolyte of the desired concentration, and the sample presaturated with the same electrolyte using a vacuum pump and placed in the sample holder. The temperatures in both reservoirs are regulated by a proportional integral differential temperature controller (EuroTherm 2216e) connected to a submerged heater (Omega VPT-107) and a cooling pump (Neslab RTE-111); the temperature difference across the sample and the temperature at the sample center are controlled independently. The electrolyte in each reservoir is stirred from the bottom using magnetic stirrers to eliminate salt precipitation. Two experimental procedures are followed for each concentration value. In the first, one reservoir is gradually heated while the other is kept at a constant temperature; in the second, one reservoir is gradually heated while the other reservoir is gradually cooled, maintaining constant midsample temperature. When a desired steady state temperature difference is achieved across the sample, it is maintained for >30 min.

The column apparatus consists of a vertical cylindrical column (Figure 1b) which is isolated thermally and electrically. The column is filled with NaCl electrolyte of the desired concentration and heated from the top using a controlled heater. The experimental procedure is to warm the fluid gradually to reach the desired temperature difference, maintaining this for >30 min. The experiments were designed to avoid convection, by imposing a thermal gradient perpendicular to gravity in the plug apparatus, and which increases upward in the column apparatus. Values of the thermoelectric coupling coefficient for the rock samples are obtained using equations (5) and (18), while the electrode effect for a given temperature difference is obtained from equation (17).

3.2. Measurements of EED Potential

The “EED” plug and column apparatus for measuring the electrochemical exclusion-diffusion potential are modified from those described above (Figures 1c and 1d). In the plug experiment, the reservoirs and sleeve are filled with NaCl electrolyte of the desired concentration, and the sample is presaturated with electrolyte from one of the reservoirs using a vacuum pump, before being placed in the sleeve. An experiment commences once each end of the rock sample faces an electrolyte of different concentration. Two sets of experiments were undertaken in the plug apparatus. In the first, the concentration of the electrolyte in one reservoir and the saturated sample was set to $0.1\ M$ and the concentration of the electrolyte in the second

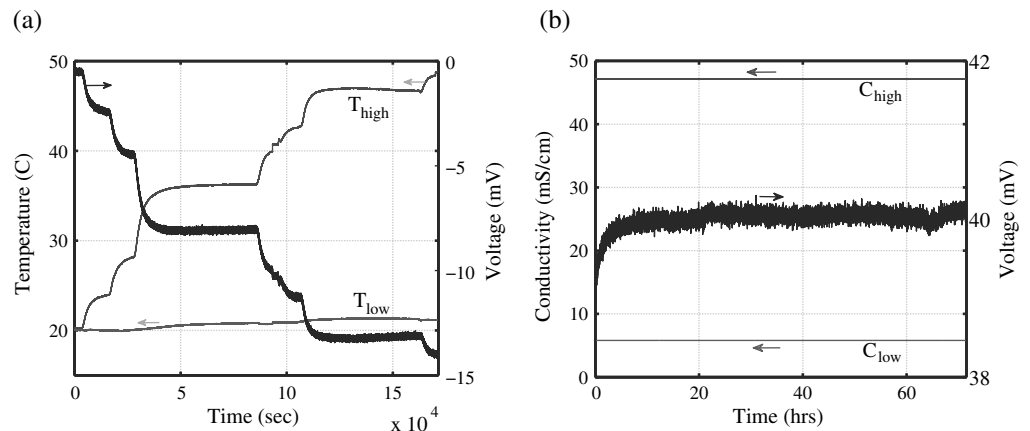


Figure 2. Typical experimental results from the column apparatus. (a) Temperature at the base (low) and top (high) of the column, and apparent thermoelectric diffusion potential including electrode effects for 0.05 M NaCl electrolyte; (b) concentration at the base (high) and top (low) of the column, and apparent electrochemical diffusion potential, at 298 K (20°C).

reservoir was varied to achieve the desired concentration ratio across the sample; in the second, the concentration of the electrolyte in one reservoir and the saturated sample was set to 0.5 M and the concentration of the electrolyte in the second reservoir was varied. In the column experiment, each compartment is filled with electrolyte of the desired concentration. A ball valve with the same diameter as the column initially separates the compartments. The valve comprises a hollow ball that is open to the lower compartment; hence, the initial separation of the fluids occurs across its top surface. Prior to commencing an experiment, the lower compartment is filled with electrolyte of higher concentration to a level above the valve to ensure no air is trapped, the valve is closed, and any excess electrolyte is carefully removed from the upper compartment. Then the upper compartment is filled with electrolyte of lower concentration, thus ensuring that the denser electrolyte is at the base of the column to avoid convective mixing. The effect of buoyancy forces on the migration of ions is neglected in our analysis. An experiment commences when the valve separating the compartments is opened; this slightly perturbs the formed contact between the fluids slightly, but the density contrast ensures the system is hydrodynamically stable. Three sets of experiments were undertaken in the column apparatus, in which the concentration of the electrolyte in the lower compartment was set to either 0.1, 0.57, or 1.11 M and the concentration of the electrolyte in the upper compartment was varied to achieve the desired concentration ratio across the column. In all experiments, the temperature is fixed at 293 K (20°C). Values of the electrochemical exclusion-diffusion potential for the rock samples are obtained using equation (19), while the electrode effect for a given concentration difference is obtained from equation (17).

4. Results

4.1. Electrode Potentials

Results obtained from a typical TE column experiment are shown in Figure 2a, and from a typical EED column experiment in Figure 2b. The difference in temperature or concentration along the column clearly induces a change in voltage, which is stable (with a noise level $<100 \mu\text{V}$) and remains constant for constant values of temperature or concentration difference. Values of stabilized voltage, obtained from numerous such experiments, are shown in Figures 3a and 3b. Voltages across the TE column were measured using eleven different electrolyte concentration values, ranging from 1×10^{-4} M to 1 M. Typically, four different experiments were conducted at each concentration value, with different imposed temperature contrasts. Once a constant temperature difference was established and the voltage stabilized, measurements were taken as the averaged reading over a time period of at least 30 min. Figure 3a presents measurements obtained for five selected concentration values. The voltage is linearly dependent on the applied temperature difference. A linear regression through the data for a given electrolyte concentration provides a good fit, with $R^2 > 0.99$. As the concentration decreases, the gradient of the regression increases. Macdonald et al. [1979] performed similar experiments on KCl electrolytes over a variety of concentration values ranging from 0.005 to 0.5 M and reported similar trends.

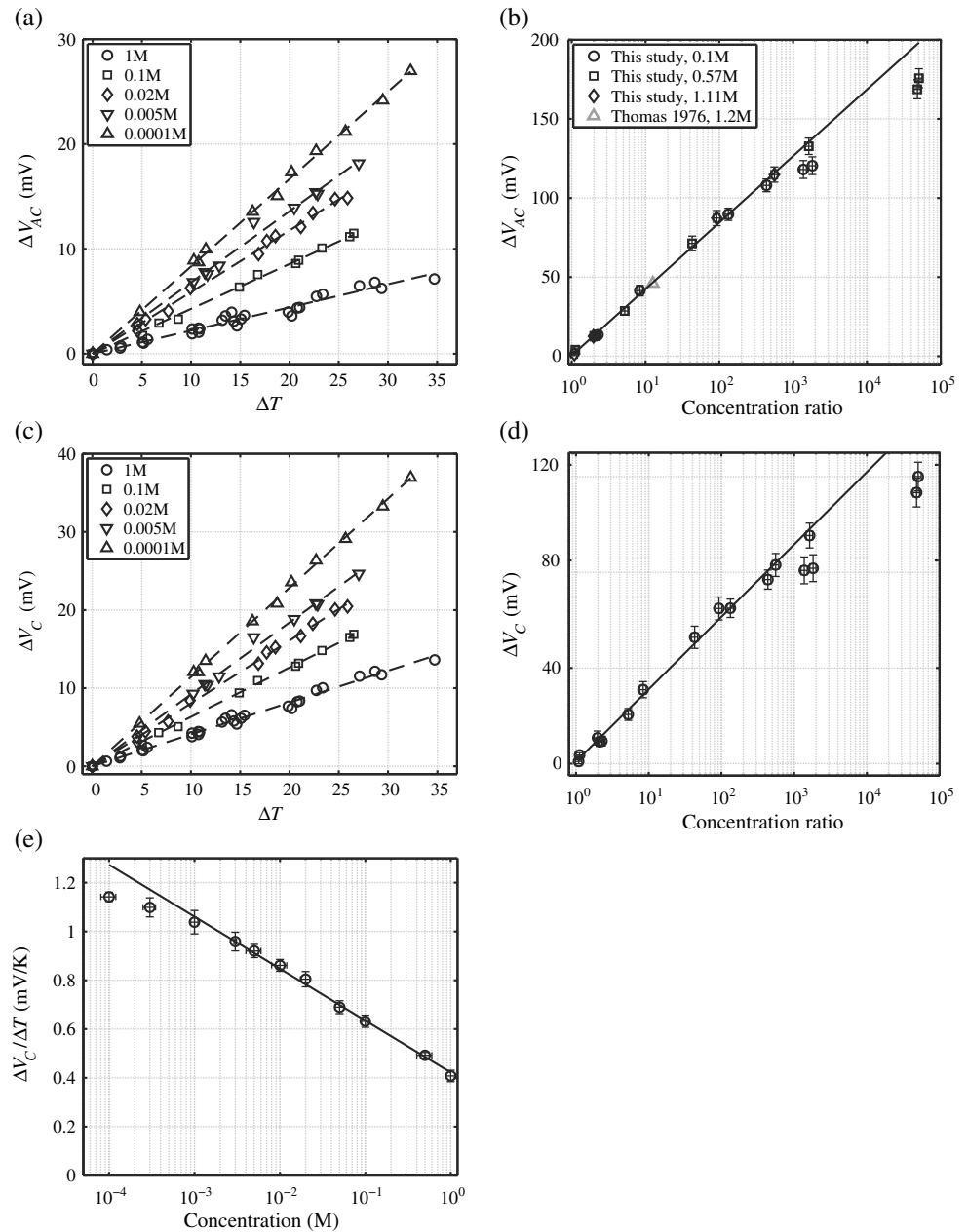


Figure 3. Summary of results from the column experiments. (a) Stabilized voltage as a function of temperature difference along the column, for a variety of NaCl electrolyte concentrations. (b) Stabilized voltage as a function of concentration difference along the column, for a fixed temperature of 298 K (20°C). Also shown is a single data point from a similar experiment by Thomas [1976] which fits the same regression. (c) Electrode temperature response, for a variety of NaCl electrolyte concentrations. The gradients of the linear regressions yield the temperature sensitivities shown in Figure 3e. (d) Electrode concentration response at 298 K (20°C). The gradient of the linear regression yields the electrode concentration sensitivity $30.34 \text{ mV decade}^{-1}$. (e) Electrode temperature sensitivity as a function of NaCl electrolyte concentration. The linear regression is given by $-0.218 \log_{10}(C) + 0.406 \text{ mV K}^{-1}$.

Voltages across the EED column were measured using three different concentration values in the high-concentration chamber; the low-concentration value was varied for each experiment. Conductivity and voltage measurements were stable and constant throughout the experiments (>60 h) and were taken as the averaged reading from the recorded signals for a given concentration ratio. Figure 3b presents the voltage measurements for each of the three high-concentration values used. The experimental measurements follow the same trend with respect to the concentration ratio regardless of the high-concentration value used;

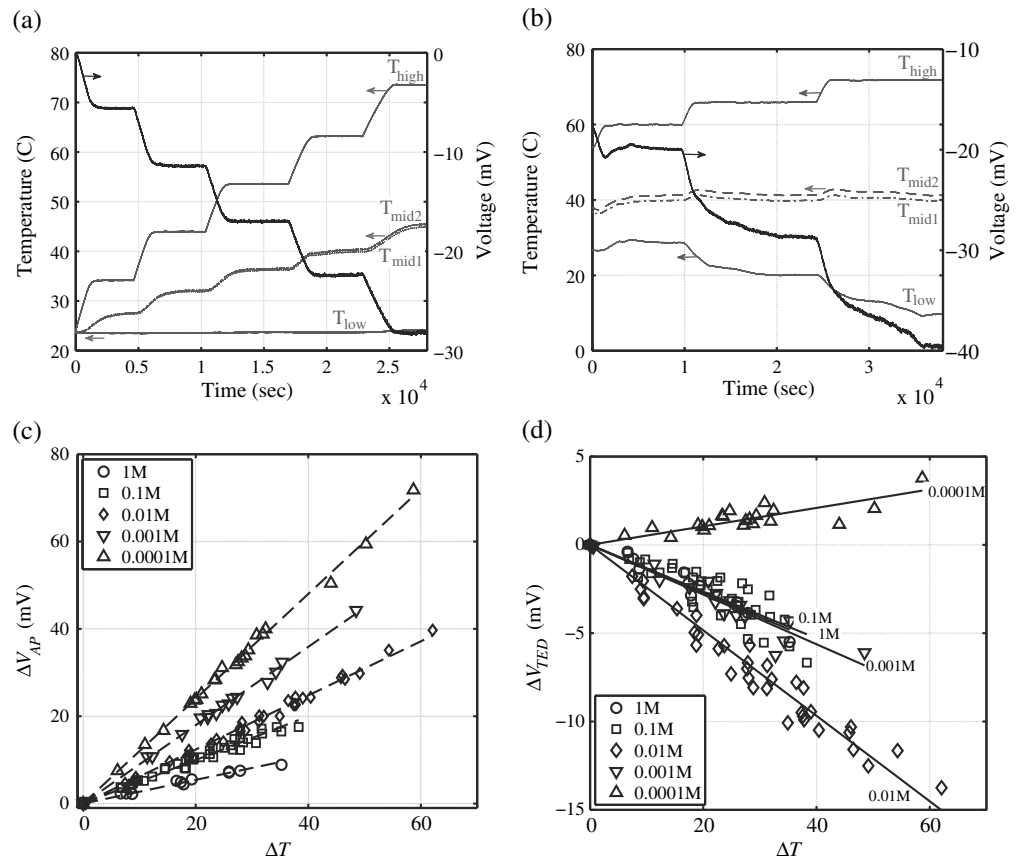


Figure 4. Typical experimental results from the plug apparatus with an imposed temperature difference. (a and b) The temperature at each end (high and low) and middle (mid1 and mid2) of the plug, and apparent thermoelectric exclusion-diffusion potential across the plug including electrode effects, for experiments performed with 0.01 M NaCl electrolyte, in which the low temperature is fixed and the high temperature is varied (Figure 4a) and the high and low temperatures are varied such as to keep the midtemperature approximately constant (Figure 4b). (c and d) Stabilized voltage as a function of temperature difference across the plug, before (Figure 4c) and after (Figure 4d) eliminating electrode effects, for a variety of NaCl electrolyte concentrations.

also shown for comparison are data from Thomas [1976]. A linear regression provides a good fit to the data, except for the highest-concentration ratio measured, with $R^2 > 0.997$, consistent with the model of Jougnot and Linde [2013]. However, the gradient of the regression is different from their model prediction which may reflect a contribution specific to the electrode material and design.

The column experimental data were used to determine the temperature and concentration sensitivity of the electrodes using equation (17) (Figures 3c and 3d). The sensitivity is linear in both cases (with $R^2 > 0.99$), except for the highest-concentration ratio measured (Figure 3d). The concentration sensitivity of the electrodes at 293 K (the only temperature investigated) is $\Delta V_c = 30.34 \log_{10}(C_1/C_2)$ mV M^{-1} for concentration ratio $C_1/C_2 < 10^3$ M (with $R^2 = 0.994$; Figure 3d). The temperature sensitivity of the electrodes is concentration dependent, given by $\Delta V_c/\Delta T = -0.218 \log_{10}(C) + 0.406$ mV K^{-1} for concentrations $C > 0.0003$ M ($R^2 = 0.996$; Figure 3e).

4.2. TED Potential

Results obtained from two typical experiments on the Doddington sample, saturated with 0.01 M NaCl electrolyte are shown in Figure 4. Figure 4a shows raw data from the first experimental procedure; Figure 4b shows raw data from the second experimental procedure. The temperature difference induced across the sample causes a change in voltage. The voltage measurements are stable with a noise level $< 100 \mu V$. Figure 4c summarizes the stabilized apparent voltages measured in the TED plug experiments. As in the column experiments, apparent voltages in the TED plug apparatus were measured using eleven different electrolyte concentration values ranging from 1×10^{-4} M to 1 M; typically, four different experiments were

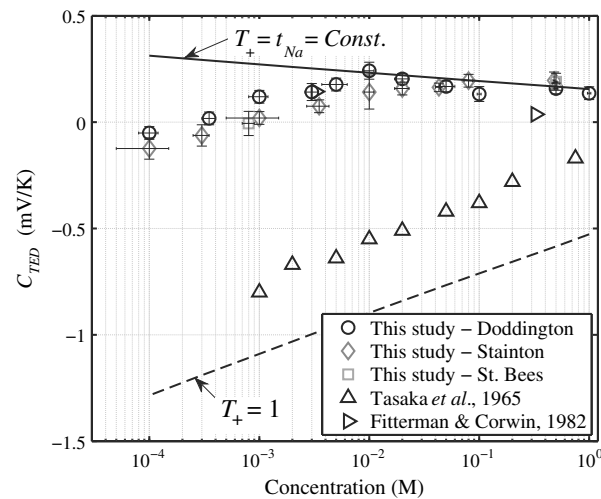


Figure 5. Thermoelectric coupling coefficient (C_{TED}) measured across our sandstone samples as a function of NaCl electrolyte concentration after accounting for electrode effects. The solid line shows the thermal diffusion coupling coefficient calculated using equations (5) and (9); the dashed line shows the thermal exclusion coupling coefficient calculated using equations (5) and (6). Also shown are data reported by *Tasaka et al.* [1965] for a cation exchange membrane saturated with KCl electrolyte, and *Fitterman and Corwin* [1982] for sandstone samples saturated with a mixed NaCl-KCl electrolyte.

sandstone samples used in this study, as a function of electrolyte concentration, after eliminating electrode effects. Also shown for comparison are measured values of the TE coupling coefficient reported in the literature (see caption for details), along with curves predicted from theory. The dashed lines show the thermal exclusion coupling coefficient calculated using equations (5) and (6), and the thermal diffusion coupling coefficient calculated using equations (5) and (9), assuming the ionic transport number of the Na ions (t_{Na}) is constant. The concentration dependence of t_{Na} was found to be negligible over the concentration range investigated. The concentration is related to activity using the activity coefficients reported by *Hamer and Wu* [1972]. Values of $Q_{\pm}^0$ and $s_{\pm}^0$ were taken from *Agar et al.* [1989] and *Lide* [2009], respectively.

The measured TE coupling coefficient is found to be negative at low electrolyte concentration and positive at high concentration, changing polarity at concentration of approximately 10^{-3} M. The largest negative measured value is -0.128 mV K^{-1} at a concentration of 10^{-4} M obtained for the Stainton sample, and the largest positive value is 0.242 mV K^{-1} at a concentration of 10^{-2} M, for the Doddington sample. At higher concentration ($>10^{-2}$ M), the measured values match, within experimental error, the predicted coupling coefficient in the limit of diffusion-dominated charge separation but deviate from this limit as the electrolyte concentration decreases. For comparison, *Tasaka et al.* [1965] measured the TE coupling coefficient across cation exchange membranes saturated with KCl electrolyte. The reported values are always negative with respect to a reference electrode at the low-temperature end of the sample, are generally larger in magnitude than those obtained in this study, and follow a trend similar to that predicted in the limit of exclusion-dominated charge separation. Moreover, *Fitterman and Corwin* [1982] measured values of the coupling coefficient across sandstone cores from Cerro-Prieto geothermal field saturated with a mixed NaCl and KCl electrolyte. The values they report are always positive and are similar in magnitude to those obtained here.

4.3. EED Potential

Typical results from the EED plug experimental apparatus are presented in Figure 6. The concentration gradient causes a change in the measured voltage, and the voltage measurements are stable within $\pm 200 \mu\text{V}$. The apparent voltage initially rises just after commencing the experiment and reaches a maximum before starting to decrease. The maximum plateau is found to be constant for typically approximately 60 min, and voltage measurements were taken as the average value over this period of time.

conducted for each concentration value. Once a constant temperature difference was established and the voltage stabilized, measurements were taken as the averaged reading over a time period of at least 30 min. Figure 4c reports measurements obtained for five selected concentration values. Similar to the column experiments (Figure 3c), the voltage is linearly dependent on the temperature difference applied and the gradient is higher as the electrolyte concentration decreases. However, after correcting for electrode effects, the thermoelectric exclusion-diffusion potential exhibits a more variable response to concentration, although the voltage response is still linearly dependent on the applied temperature difference, with R^2 varying from 0.76 to 0.95 (Figure 4d).

The ratio of the TE potential to the temperature difference (i.e., the gradient of the linear regression shown in Figure 4d) yields the thermoelectric coupling coefficient (equation (5)); Figure 5 shows the TE coupling coefficient measured across the natural

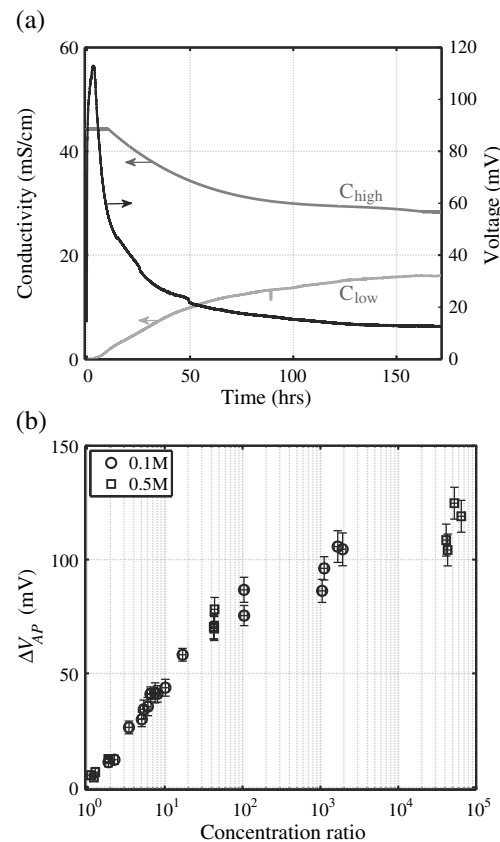


Figure 6. Typical experimental results from the plug apparatus with an imposed concentration difference. (a) Concentration at each end of the plug (high and low) and apparent electrochemical exclusion-diffusion potential across the plug including electrode effects; (b) stabilized apparent voltage as a function of concentration difference across the plug, for two different concentrations of the electrolyte saturating the sample.

EED potential is positive and becomes increasingly positive as the concentration ratio increases, reaching a maximum of +21.8 mV at a concentration of 100; moreover, up to this concentration ratio, the measured potentials match, within experimental error, the predicted EED in the limit of diffusion-dominated charge separation predicted using equation (15). However, at higher-concentration ratio, the measured values diverge from the diffusion-dominated limit and move toward the predicted EED in the limit of diffusion-dominated charge separation predicted using equation (14). At the highest-concentration ratios investigated, the measured EED potential is negative (up to −9.1 mV) or zero within experimental error. The experimental measurements follow the same trend regardless of whether the sample was initially saturated with 0.1 M electrolyte or 0.5 M electrolyte, which suggests that it is the concentration ratio between the saturated sample and the adjacent reservoir that dictates the measured EED potential, rather than the concentration of the saturating electrolyte.

Also shown in Figure 7 are data reported by Hill and Milburn [1956] and Ortiz *et al.* [1973] measured across a variety of shaley sandstone and shale samples saturated with NaCl electrolyte. Hill and Milburn [1956] did not explain how electrode effects were accounted for in their experiments; Ortiz *et al.* [1973] accounted for electrode effects using a similar method to that reported here.

5. Discussion

5.1. Concentration Dependence of the TED and EED Potentials

The measured thermal and electrochemical exclusion-diffusion potentials reported here show a strong dependence on concentration, and concentration ratio, respectively. At low concentration and concentration

Figure 7 shows the EED potential after correcting for electrode effects, as a function of the electrolyte concentration ratio. Also shown are measured values of the EED potential reported in the literature (see caption for details), along with curves predicted from theory. The dashed and solid lines shows the electrochemical exclusion potential calculated using equation (14), and the electrochemical diffusion potential calculated using equation (15), assuming the ionic transport number of the Na ions (t_{Na}) is constant, respectively. The electrolyte concentration ratio is given by C_1/C_2 , where C_1 and C_2 are the electrolyte concentrations in the reservoirs on each side of the sample, or the compartments in the column, and $C_1 > C_2$. We present the results in this way because it is clear that the exclusion and diffusion potentials depend upon the logarithm of the activity ratio (and, hence, the concentration ratio; see equations (14) and (15)). When necessary, we relate concentration ratio to activity ratio using the activity coefficients reported by Hamer and Wu [1972].

As the concentration ratio approaches unity, the concentration difference between the electrolytes approaches zero, and as the concentration ratio increases, the concentration difference also increases.

At low-concentration ratio, the measured

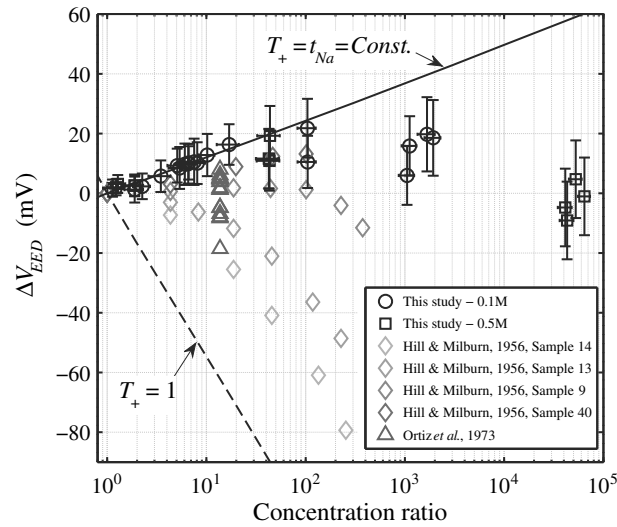


Figure 7. Electrochemical exclusion-diffusion potential (ΔV_{EED}) measured across our sandstone samples as a function of NaCl electrolyte concentration ratio, accounting for electrode effects. Also shown are measured data (various grey symbols) reported by Hill and Milburn [1956] and Ortiz *et al.* [1973] on shaly sands. The dashed line shows the electrochemical exclusion potential calculated using equation (14); the solid line shows the electrochemical diffusion potential calculated using equation (15), which assumes that the ionic transport number of the Na ions (t_{Na}) is constant.

ratio, the measured TED and EED coincide with the values predicted in the limit of diffusion-dominated charge separation, which are positive with respect to a reference electrode at the low-temperature or low-concentration side of the sample, consistent with charge separation resulting from the migration of relatively more mobile chloride ions down the temperature or concentration gradient. At intermediate values of concentration and concentration ratio ($10^{-2} M$ and 100, respectively), the measured TED and EED begin to deviate from the diffusion-dominated limit and move toward the exclusion-dominated limit, which is negative with respect to a reference electrode at the low-temperature or low-concentration side of the sample, consistent with the exclusion of (negatively charged) chloride ions from the pore space and migration of sodium ions down the temperature or concentration gradient. This, in turn, is consistent with negatively charged mineral surfaces in our quartz-

dominated sandstone samples as has been observed in numerous previous studies [e.g., Hunter, 1981 and references therein; Jouniaux and Pozzi, 1995, 1997; Revil *et al.*, 1999; Dove and Craven, 2005; Vinogradov *et al.*, 2010]. The measured exclusion-diffusion potentials fall to zero at a critical concentration or concentration ratio, suggesting that exclusion and diffusion potentials of opposite sign exactly cancel.

5.2. Comparison of Macroscopic Hittorf Number From TED and EED Measurements

Figure 8 shows the macroscopic Hittorf transport number calculated for each measured value of TED and EED using equations (4) and (13), plotted against concentration. For the EED experiments, in which concentrations vary across the sample, the Hittorf numbers are plotted against the geometric mean concentration. The Hittorf numbers follow a similar trend regardless of whether they were obtained from measurements of TED or EED and, for a given value of concentration, are largely the same within experimental error. At high concentration, measured values correspond with the value of $T_+ = t_{Na}$, consistent with charge separation dominated by diffusion. At concentrations lower than approximately $10^{-2} M$, the Hittorf numbers diverge from the diffusion-dominated limit and increase in value toward the exclusion-dominated limit of $T_+ = 1$. Thus, it is clear that charge exclusion plays a significant role in generating the measured exclusion-diffusion potentials in sandstones at low concentration. However, the Hittorf transport number does not explicitly include information about rock texture.

Also shown in Figure 8 are values of the Hittorf number predicted using the model of Revil and Jougnot [2008] for various values of the cation exchange capacity (CEC). The curves are given by

$$T_+ = \frac{t_+ (\sqrt{1 + R^2} + R)}{t_+ (\sqrt{1 + R^2} + R) + t_- (\sqrt{1 + R^2} - R)} \quad (21)$$

with

$$R = \frac{\rho_g}{2eC} \frac{1 - \phi}{\phi} (1 - f_Q) \text{CEC} \quad (22)$$

where ρ_g is the grain density, ϕ the porosity, and f_Q represents the fraction of the countercharge that resides in the Stern layer. The parameter R represents the ratio of surface to bulk (electrolyte) electrical conductivity. We use an approximated value of 0.2 for the porosity of our samples, reported in Table 3 and use the value of 0.8 for f_Q , based on Leroy and Revil [2009]; the CEC is constant for a given curve, but curves are generated for CEC over the

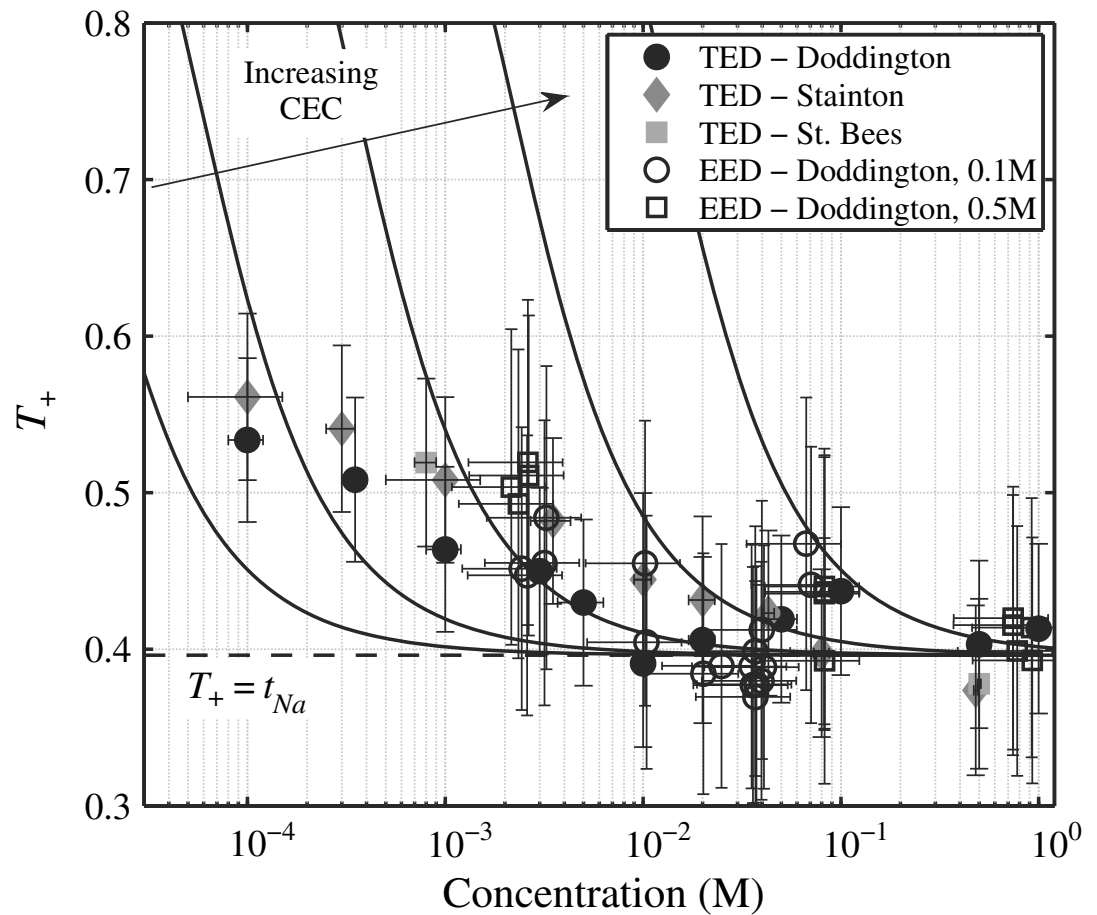


Figure 8. Hittorf transport numbers as a function of concentration. The geometric mean concentration is used in experiments where a concentration difference is imposed. The curves are obtained from the model of *Revil and Jougnot* [2008] for CEC values in the range 10^{-6} – 10^{-3} meq L^{-1} .

range of 10^{-6} – 10^{-3} meq L^{-1} . The model-predicted curves are qualitatively similar to the experimental data; as the electrolyte concentration (C) decreases, so the curves depart from the diffusion-dominated limit, with the departure occurring at higher-concentration values with decreasing CEC. However, the quantitative match is poor: the experimental data do not follow the shape of the curves. Further work is required to understand this. One possible explanation is that the CEC and/or f_Q is concentration dependent, so it is not appropriate to assume a constant value; another is that the Hittorf transport number does not explicitly include information about rock texture, which we investigate in the next section.

5.3. Effect of Rock Texture and Electrolyte Concentration

The exclusion-diffusion potential arising from a concentration gradient across a charged porous medium was investigated by *Westermann-Clark and Christoforou* [1986] using a simple capillary tube model. For a given ionic mobility contrast and specific surface charge, they calculated the relative contribution of the exclusion and diffusion potentials as a function of r/λ , where λ is the Debye length and r is the radius of the capillary. The Debye length is a measure of the thickness of the electrical double layer at the solid-electrolyte interface which, in a 1-1 electrolyte, is given by [e.g., *Revil et al.*, 1999]

$$\lambda = \left(\frac{\epsilon k_B T}{2000 N_A C e^2} \right)^{\frac{1}{2}} \quad (23)$$

where N_A is Avogadro's number and ϵ is the electrolyte permittivity. *Westermann-Clark and Christoforou* [1986] found that the exclusion-diffusion potential in a capillary tube is dominated by the exclusion potential when r/λ is small (<0.1 – 1) and by the diffusion potential when r/λ is large (>10 – 100). It is also dominated by the diffusion

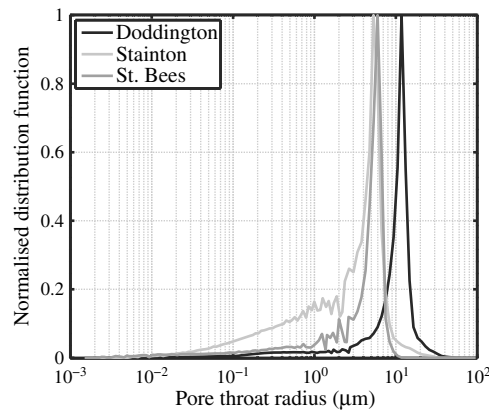


Figure 9. Frequency distribution of pore throat radius measured in the Doddington, Stainton, and St. Bees sandstone samples.

potential when the surface electrical charge is small. When r/λ is small, the electrical double layer occupies most of the capillary, so there is significant charge exclusion from the capillary, and the exclusion potential dominates. Conversely, when r/λ is large, the electrical double layer is small relative to the capillary radius, so there is little charge exclusion, and the diffusion potential dominates. The exact value of r/λ for which the exclusion or diffusion potential dominates depends on the electrical charge on the solid surface and the relative mobility of the anions and cations. When the specific surface charge is small, there is also little charge exclusion from the capillary so the diffusion potential dominates.

We investigate the relative contribution of exclusion and diffusion potentials by calculating the exclusion efficiency

$$\eta = \frac{T_+ - t_{Na}}{1 - t_{Na}} \quad (24)$$

as a function of r/λ , where T_+ is the macroscopic Hittorf transport number calculated from our thermoelectric and electrochemical potential measurements (Figure 8) and r is the modal pore radius measured on our sandstone samples using the mercury injection method (Figure 9). When calculating λ , the geometric mean concentration is used, and the concentration dependence of the electrolyte permittivity is accounted for using

$$\varepsilon = 8.85 \times 10^{-12} (80 - 13C + 1.065C^2 - 0.03006C^3) \quad (25)$$

where concentration is in M and permittivity is in $F\ m^{-1}$ [Malmberg and Maryott, 1956]. The exclusion efficiency is unity when the exclusion-diffusion potential is dominated by the exclusion potential ($T_+ \rightarrow 1$) and zero when the exclusion-diffusion potential is dominated by the diffusion potential ($T_+ \rightarrow t_{Na}$).

Figure 10a shows that the exclusion efficiency obtained from our measurements of the exclusion-diffusion potential is zero at large values of r/λ , so the diffusion potential dominates but deviates from zero as r/λ decreases. Values obtained from the TED measurements, and the EED measurements in plugs saturated with 0.1 M electrolyte, lie mostly on the same trend within experimental error; however, values obtained from the EED measurements in plugs saturated with 0.5 M electrolyte do not fit as well. The model of Revil and Jougnot [2008] discussed previously does not yield a good fit to the experimental data (Figure 10b), so we choose instead to fit the simple linear regression shown in Figure 10a. Overall, the value of r/λ above which the diffusion potential dominates is approximately 4000 (i.e., the pore radius must be approximately 4000 times larger than the Debye length for exclusion potentials to be negligible), and exclusion potentials contribute approximately 30% of the total exclusion-diffusion potentials at the lowest concentration measured. The value of r/λ above which diffusion dominates is higher than that predicted by Westermann-Clark and Christoforou [1986], which suggests that exclusion potentials in rocks such as sandstones become important at significantly higher concentration (i.e., smaller Debye length) and/or larger pore size than expected based on a simple capillary tube model. This may reflect the important role played by the smallest pores and throats in impeding the passage of cocharge through the pore space.

5.4. Comparison With the Results of Leinov et al. [2010]

We calculated the limiting cases of an exclusion-dominated thermoelectric potential, and a diffusion-dominated thermoelectric potential, using equations (6) and (9), respectively. Leinov et al. [2010] also presented versions of these two equations that allowed comparison with their experimental data (their equations (15) and (16)) and shifted the value of the second term in their equation (15), which represents the intercept at an electrolyte concentration of 1 M , to match their experimental data at low electrolyte concentration (see their Figure 4b). We have not imposed this shift when calculating the thermal diffusion potential shown in Figure 5, or the exclusion efficiency shown in Figure 10.

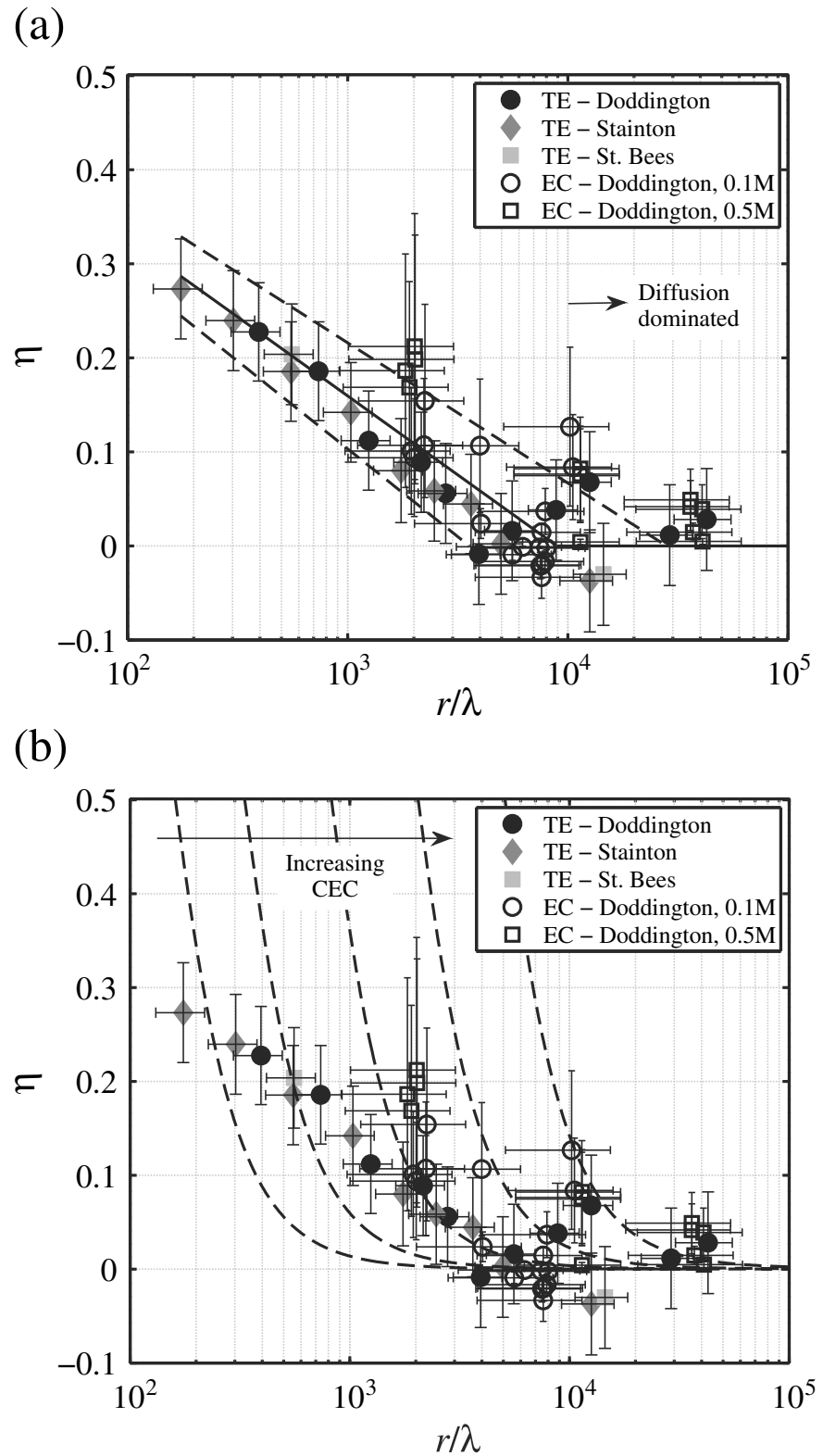


Figure 10. Exclusion efficiency (η) as a function of dimensionless pore throat radius (r/λ) calculated from the macroscopic Hittorf transport numbers reported in Figure 8. (a) The regression shown is given by $\eta = -0.1679 \cdot \log_{10}(r/\lambda) + 0.6633$ for $r/\lambda \leq 9 \times 10^3$, and $\eta = 0$ for $r/\lambda > 8.912 \times 10^3$, with $R^2 = 0.738$. Dashed lines show the 90% confidence interval for the linear regression. (b) The experimental data are compared to the model of Revil and Jougnot [2008] for CEC values in the range 10^{-6} – 10^{-3} meq L $^{-1}$.

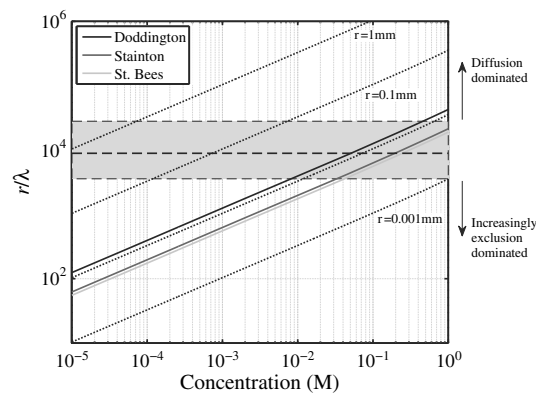


Figure 11. Dimensionless pore throat radius (r/λ) as a function of electrolyte concentration (M) for values of pore throat radii suitable for sandstones [Bourbie and Zinszner, 1985; Doyen, 1988]. Solid lines correspond to the sandstone samples used here. Also shown is the threshold value of dimensionless pore throat radius, based on the experimental data reported here, above which exclusion-diffusion potentials are dominated by diffusion and ionic exclusion from the pore space can be neglected.

Leinov et al. [2010] argued that their measured values of thermoelectric potential closely match the diffusion-dominated limit at high values of electrolyte concentration (when r/λ is large), and we reach a similar conclusion here. However, they also argued that their measured values closely match the exclusion-dominated limit at low values of electrolyte concentration, after adjusting the value of the second term of their equation (15). After adjustment, their results suggested that there is only a narrow range of electrolyte concentration over which the thermoelectric potential is not dominated by either diffusion or exclusion. *Leinov et al.* [2010] justified this adjustment by observing that a similar approach was adopted by *Tasaka et al.* [1965] to match their experimental data measured across laboratory membranes which exhibit close to perfect behavior (all cocharge excluded from the pore space). Here we suggest that this adjustment was not appropriate: the

measured data of *Leinov et al.* [2010] do not closely match the exclusion-dominated limit at low values of electrolyte concentration. Rather, there are only small deviations of their measured potentials from the diffusion-dominated limit. These deviations are observed at the lowest electrolyte concentrations investigated which, in the relatively high permeability sandstone samples used in their experiments, corresponds to relatively large values of r/λ (Figure 10). It is likely that thermoelectric potentials across sandstones and other geological porous media will approach the exclusion-dominated limit at smaller values of r/λ ; however, experimental data to confirm this prediction have not yet been obtained.

5.5. Importance of Eliminating Electrode Effects

Temperature- and concentration-dependent electrode effects make a significant contribution to the apparent voltages measured across rock samples with an imposed temperature or concentration gradient and, indeed, may dominate the measured potentials. For example, electrode temperature sensitivities reported here ($0.4\text{--}1.15\text{ mV K}^{-1}$) are larger in magnitude than the thermoelectric coupling coefficient we measured in sandstone (up to 0.25 mV K^{-1} ; Figure 5); similarly, electrode concentration sensitivities reported here ($30.34\text{ mV decade}^{-1}$) are larger in magnitude than the electrochemical exclusion-diffusion potentials (up to $8.69\text{ mV decade}^{-1}$). Thus, it is essential to eliminate the electrode sensitivity to temperature and concentration differences prior to interpreting measurements to determine the exclusion-diffusion potential in which electrodes are immersed in electrolyte of differing temperature or concentration. Few previous studies report the approach used to eliminate these effects, and many report exclusion-diffusion potentials that include electrode effects (Tables 1 and 2).

5.6. Implications for SP Measurements for Subsurface Geophysical Monitoring

Exclusion-diffusion potentials arising from temperature gradients are widely neglected in SP surveys, despite the ubiquitous presence of temperature gradients in subsurface settings such as volcanoes and hot springs, geothermal fields, and oil reservoirs during production via water or steam injection [e.g., *Fitterman and Corwin*, 1982; *Darnet et al.*, 2004; *Jardani et al.*, 2007, 2008; *Byrdina et al.*, 2009; *Jardani and Revil*, 2009; *Revil et al.*, 2003, 2008, 2013; *Ishido*, 2004; *Legaz et al.*, 2009; *Finizola et al.*, 2010; *Vandemeulebrouck et al.*, 2010; *Gulamali et al.*, 2011]. Likewise, with the exception of borehole SP logging, exclusion-diffusion potentials arising from concentration gradients are also neglected or, at best, it is assumed that the diffusion potential dominated. To better interpret these SP sources requires well-constrained measurements or models of the various coupling terms. Our results show that Hittorf transport numbers are the same within experimental error regardless of whether ion transport occurs in response to concentration or temperature gradients, allowing predictions of the contribution of TED potentials from EED potential measurements, and vice versa.

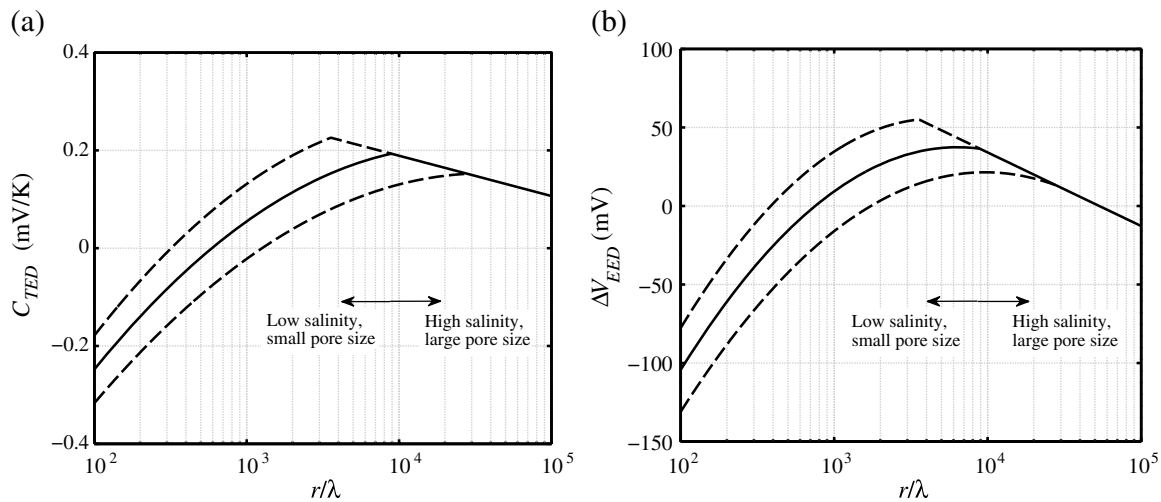


Figure 12. Predicted values of (a) thermoelectric coupling coefficient (C_{TED}) and (b) electrochemical exclusion-diffusion potential (ΔV_{EED}) as a function of dimensionless pore throat radius (r/λ), calculated using the exclusion efficiency (Figure 10) along with the end-member values of exclusion- and diffusion-dominated potentials (Figures 5 and 7). Dashed lines show the 90% confidence interval for the linear regression in Figure 10a.

Moreover, they suggest that the diffusion potentials will dominate only if the pore throat radius is more than approximately 4000 times larger than the diffuse layer thickness. In fine-grained sandstones with small pore throat diameter, this condition is likely to be met only if the saturating brine is of relatively high salinity (Figure 11); thus, in many cases of interest to earth scientists, thermoelectric, and electrochemical exclusion-diffusion potentials will comprise significant contributions from both ionic diffusion through, and ionic exclusion from, the pore space of the rock. However, in coarse-grained sandstones, or sandstones saturated with high-salinity brine, thermoelectric and electrochemical exclusion-diffusion potentials can be described using end-member models in which ionic exclusion is neglected. Our experimental data do not probe the region where exclusion potentials dominate.

Finally, we can use the exclusion efficiency shown in Figure 10, along with the end-member values of exclusion- and diffusion-dominated potentials (Figures 5 and 7) to predict the TED and EED as a function of r/λ for sandstones saturated with NaCl electrolyte (Figure 12). We find that the predicted behavior depends upon pore size and salinity in a complex way. At low values of r/λ (corresponding to low salinity and/or large pore size), the thermoelectric coupling coefficient is negative (Figure 12a) as is the electrochemical exclusion-diffusion potential (Figure 12b). As r/λ increases, C_{TED} and V_{EED} both increase in magnitude, crossing zero at a value of $r/\lambda = 591$ in the case of C_{TED} and $r/\lambda = 752$ in the case of V_{EED} . Further increases in r/λ (corresponding to increasing salinity and/or decreasing pore size) yield positive values of C_{TED} and V_{EED} , which increase in magnitude until a maximum is reached, at a value of $r/\lambda = 8912$ in the case of C_{TED} , and $r/\lambda = 6336$ in the case of V_{EED} . Values of C_{TED} and V_{EED} then decrease in magnitude, falling to zero again in the case of V_{EED} when $r/\lambda = 53370$ and then becoming increasingly negative again. Thus, C_{TED} and V_{EED} may be positive, negative, or zero depending upon sandstone rock texture (expressed here by r) and salinity (expressed by λ). It is interesting to note that the value of C_{TED} estimated by *Revil et al.* [2013] of 0.5 mV K^{-1} , based on data from a sandbox experiment in which electrode effects did not need to be corrected for, is reasonably consistent with the diffusion-dominated value for NaCl electrolyte at very low concentration (Figure 5). Diffusion potentials may dominate even at low concentration in a sandpack, in which the pore radius r is likely to be large compared to the consolidated samples investigated here.

6. Conclusions

Thermoelectric and electrochemical exclusion-diffusion potentials have been measured across sandstone samples saturated with NaCl electrolyte using a new experimental method that explicitly accounts for temperature- and concentration-dependent electrode effects. We find that electrode effects can dominate the apparent voltages measured across rock samples with an imposed temperature or concentration

gradient; thus, it is essential that these effects are eliminated prior to interpreting voltage measurements to determine the exclusion-diffusion potential. After correcting for electrode effects, we find that Hittorf transport numbers are the same within experimental error regardless of whether ion transport occurs in response to temperature or concentration gradients, allowing prediction of the thermal exclusion-diffusion potentials from electrochemical exclusion-diffusion potential measurements, and vice versa. Moreover, diffusion potentials in sandstones saturated with NaCl brine dominate only if the pore throat radius is more than approximately 4000 times larger than the diffuse layer thickness. In fine-grained sandstones with small pore throat diameter, this condition is likely to be met only if the saturating brine is of relatively high salinity; thus, in many cases of interest to earth scientists, exclusion-diffusion potentials will comprise significant contributions from both ionic diffusion through, and ionic exclusion from, the pore space of the rock. However, in coarse-grained sandstones, or sandstones saturated with high-salinity brine, exclusion-diffusion potentials can be described using end-member models in which ionic exclusion is neglected. Exclusion-diffusion potentials in sandstones depend upon pore size and salinity in a complex way: they may be positive, negative, or zero depending upon sandstone rock texture (expressed here by the pore radius r) and salinity.

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Data supporting Figures 3, 4, 6, and 9 are available as in supporting information Tables S1–S5. The authors thank the referees, the associate editor, and the editor for their constructive reviews.

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