Electro-osmosis in gels: Application to Agar-Agar

Fabien Cherblanc *, Jérôme Boscus, Jean-Claude Bénet

Laboratoire de mécanique et génie civil, UMR CNRS 5508, Université Montpellier 2, CC 048, place Eugène Bataillon, 34095 Montpellier, France

Abstract

Widely used in food- and bio-engineering as a reference material, Agar-Agar gel is the focus of an experimental investigation concerning the electro-osmosis phenomenon. After presenting the experimental methods, one trial is discussed in detail. A fair reproducibility of results is obtained, and the averaged electro-osmotic permeability is provided. This value lies in the range generally measured on various kind of soils, even if Agar-Agar gel does not share any micro-structural characteristics with soils. *To cite this article: F. Cherblanc et al., C. R. Mecanique 336 (2008).*
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Résumé

Electro-osmose dans les gels : Application au gel d'Agar-Agar. Largement utilisé en bio-ingénierie comme un matériau modèle, le gel d'Agar-Agar est l'objet d'une étude expérimentale relative au phénomène d'électro-osmose. Après la présentation des méthodes expérimentales, un essai est discuté en détail. Une bonne reproductibilité des résultats est observée, et une valeur moyenne de la perméabilité électro-osmotique du gel d'Agar-Agar est proposée. Ce résultat est en accord avec la plage de valeurs mesurées sur une large gamme de géo-matériaux, même si les caractéristiques micro-structurales du gel d'Agar-Agar sont très éloignées de celles d'un sol. *Pour citer cet article : F. Cherblanc et al., C. R. Mecanique 336 (2008).*
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1. Introduction

Many geological and biological media (clays, cartilages, ...) exhibit swelling-shrinkage behaviour when submitted to hydraulic, electric or osmotic stresses. Since similar theoretical approaches are involved, the coupling between the mechanical behaviour and transport phenomena is of great interest in geomechanical and biomedical engineering [1]. The strains observed stem from liquid phase transport phenomena that take place in porous media (osmosis, electro-osmosis). These coupling effects observed at the macroscale generally results from the electrical interactions at the

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* Corresponding author.
  E-mail address: chb@lmgc.univ-montp2.fr (F. Cherblanc).

microscale [2]. The link between these two scales of description and the physical properties associated can be derived theoretically using an upscaling procedure [3], but also relies on a macroscopic experimental characterization since the microscopic quantities are hardly measurable.

When a porous medium saturated by an ionic solution exhibits some fixed electrical charges at the surface of the solid phase, the spatial distribution of ions and cations in the liquid phase is ruled by the electrical double layer theory [2]. If the fixed charges are negatives, excess mobile cations are required in the solution to ensure electroneutrality. When submitted to an external electric field, these excess mobile cations exert an additional momentum to the pore fluid that drives the liquid phase toward the cathode. This net movement of fluid relative to the solid structure under an imposed electric potential gradient is called electro-osmosis [4]. In practice, the electro-osmotic velocity is described at a macroscopic scale by

$$\mathbf{v}_L = -k_E \nabla \Phi \qquad (1)$$

where $\mathbf{v}_L$ is an averaged velocity also called Darcy's velocity or filtration velocity, and Φ is the electrical potential. The electro-osmotic permeability, k_E, characterizes the porous medium by relating the flux $\mathbf{v}_L$ to the force $\nabla \Phi$. This relation can also be derived theoretically from the linear thermodynamics of irreversible processes (TIP) ideas [5]. Electro-osmotic permeability of soil has been widely investigated in the civil engineering area since some potential applications in hazardous waste management are based on electrokinetic phenomena [6,7]. For a large panel of soils, from clay to sand, the practical range of electro-osmotic permeability lies between 1×10^{-9} to 1×10^{-8} m^2 V^{-1} s^{-1}, while the hydraulic permeability can range over 6 decades [2,8]. This makes it possible some interesting application in clays, since a pressure-induced liquid flow can hardly be obtained in such low-permeable medium. While geological porous media have received a great deal of attention, little results are available about gels. Thereby, this contribution presents an experimental investigation dealing with the electro-osmotic characterization of Agar-Agar gel.

2. Materials

Gels are usually assumed to be a cross-linked polymer-based network saturated with a liquid phase. The solid matrix ensures the gels holding excellent mechanical properties while the large water content makes it possible the transport of diffusive ions. Gels are able to convert the chemical, electrical and thermal energy to the mechanical energy easily, what makes them a very competitive candidate in the development of artificial muscles, sensors/actuators [9]. Their physical properties similar to articular cartilages account for their large use in tissue engineering [10].

Agar-Agar is typically a strong gelling component widely used in the food industry as a thickening agent (E406), a vegetarian gelatin substitute, or a clarifying agent in brewing. Agar is an unbranched polysaccharides extracted from the cell walls of some species of red algae or seaweed. It can be considered as an heterogeneous mixture of two classes of polysaccharides: agaropectin and agarose. Although both polysaccharides classes share the same galactose-based backbone, agaropectin is heavily modified with acidic side-groups, such as sulfate and pyruvate [11]. The neutral charge and lower degree of chemical complexity of agarose makes it less likely to interact with biomolecules, such as proteins. This confers to agarose the ability of being used as a culture medium for microbiological work and electrophoretic identification of proteins in DNA sampling.

Gel samples are prepared by dissolving dehydrated agar powder in hot water with a 7% mass ratio, and heating the solution at 90 °C to have an homogeneous and random distribution of agar molecules in the solution. Gelation occurs by cooling the agar solution to a temperature below the gelation point estimated around 45 °C [11]. In the widely accepted *double helix* model, agar chains are cross-linked to each other by forming a double helix of 1.9 nm pitch. The resulting 3D polymeric network has a microscopic characteristic length about 0.2 μm [12,13]. The final water content, measured by differential weighing after 48-hours drying at 105 °C, is 1300%. The solid structure exhibits some electrical negative charges resulting from the ionization of acidic groups carried by agaropectin chains; Agar-Agar is generally described as a polyelectrolyte gel. Consequently, Agar-Agar gel should be sensitive to electrokinetic phenomena, what is the scope of the next section dealing with the experimental characterization of the electro-osmotic permeability.

3. Experimental device

The complete experimental device is given in Fig. 1. The Agar-Agar gel sample (a) (64 mm diameter and 26 mm thick) is held between two parallels perforated Plexiglas plates (b) (64 mm diameter and 5 mm thick). These plates
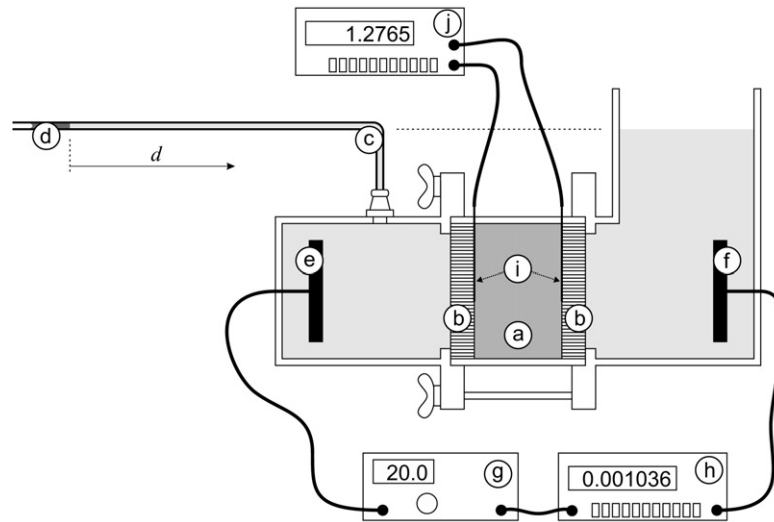
Fig. 1. Experimental device for the determination of the electro-osmotic permeability of Agar-Agar gel sample.
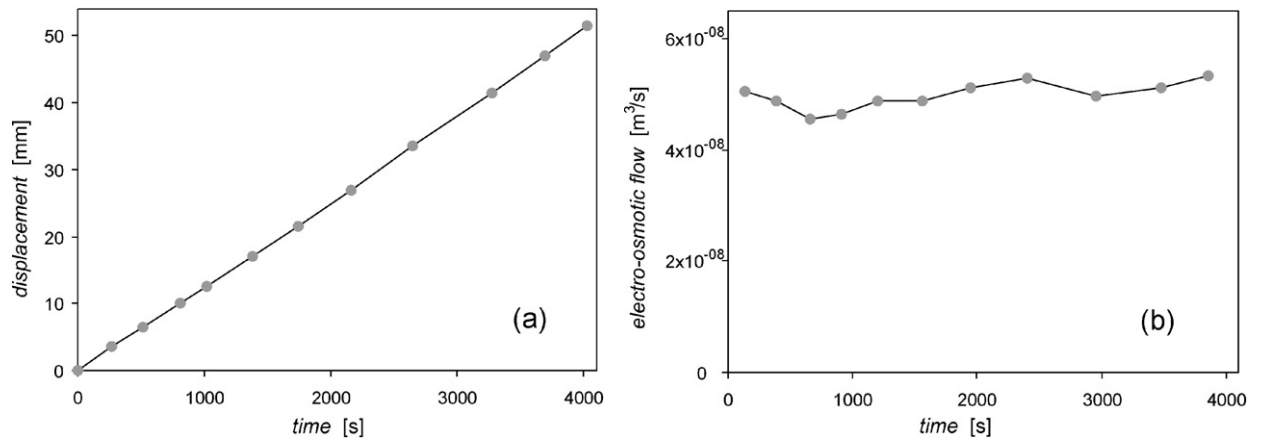

Fig. 2. Experimental results with a 26 mm thick sample submitted to a 10 V electrical potential difference: (a) oil bubble displacement as a function of time, (b) electro-osmotic flowrate through the sample as a function of time.

applied a slight axial compression stress on the gel sample to ensure the no-flow condition on the periphery. The whole system is saturated by pure distilled water.

The capillary tube on the left (c) is used to determine the water flow through the sample. A 4 mm diameter tube allows us to measure very low fluxes (Fig. 2) while the water evaporation is prevented by disposing an oil bubble on the left edge (d). The suction resulting from capillary effects at the water-oil interface is fairly negligible. For one experimental measure, the electro-osmotic flux in the sample causes an horizontal displacement, d, of water in the capillary tube less than 15 cm. This corresponds to a water rise in the right tank about 0.1 mm, which is not sufficient to create some pressure gradient discrepancies.

To impose an electrical potential gradient through the gel sample, two electrodes (anode on the left (e) and cathode on the right (f)) are immersed in each water tank. They are connected to a controlled voltage generator (g) via an amperometer (h). These electrodes are made of carbon cloth to take advantage of the inert characteristic of carbon with respect to water. A second electrical circuit is used to measure the effective electrical gradient. It is composed of two platinum electrodes (i), each of them is stuck between the porous plate and the sample. These electrodes are connected to a high impedance voltmeter (j).
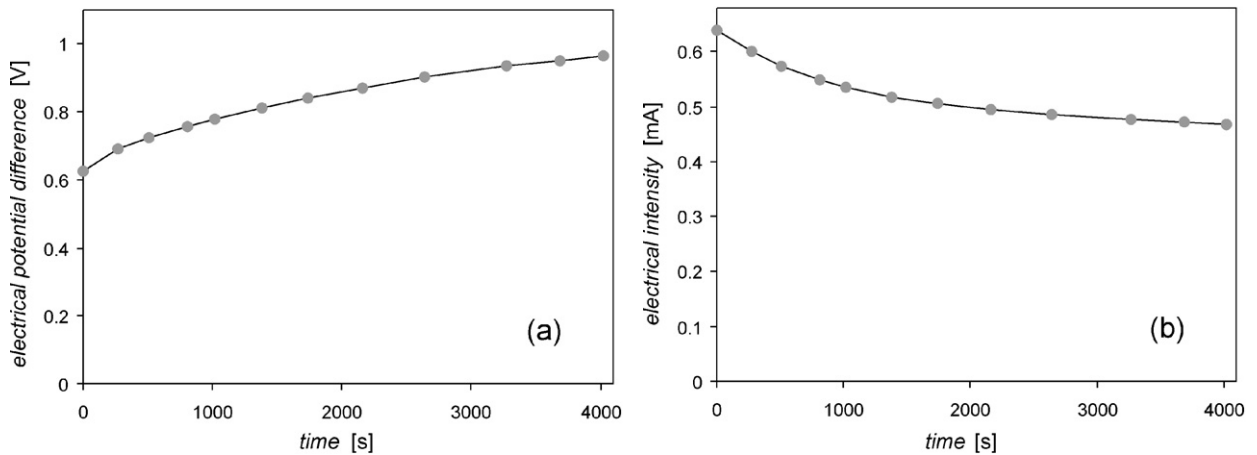
Fig. 3. Experimental results with a 26 mm thick sample submitted to a 10 V electrical potential difference: (a) electrical potential difference between both sides of the sample, (b) ionic current intensity through the sample.

The time required for one experimental measure is less than 1 hour, while the electrical intensity is always lower than 1 mA. Thus, the gas volume of oxygen produced by electrolysis at the anode is negligible and does not lead to some discrepancies while estimating the liquid flow rate through the sample.

The experimental procedure is relatively straightforward. Imposing an electrical potential difference between both electrodes (e)–(f) generates an electrical gradient inside the gel sample. The electro-osmotic flow produced is evaluated through the measure of the oil bubble displacement. Some experimental results are presented in the next section.

4. Results and discussion

With a 10 V potential difference applied between electrodes, the experimental measures are given below. The oil bubble displacement, d, is given in Fig. 2(a). Using a centered finite difference scheme, the corresponding water flow rate is computed in Fig. 2(b). The derivation operator amplifies the measurement errors, what explains the observed fluctuations. Anyway, a smoothed trend curve could easily be plotted inside the confidence intervals.

While the electrical potential difference applied between the carbon electrodes (e)–(f) is regulated at 10 V, the electrical potential difference effectively applied at the boundaries of the sample is measured using the platinum electrodes (i) (Fig. 3(a)). A slight increase was always observed. Indeed, due to the water electrolysis, water in the right tank gets acid, while it gets basic in the left tank; this increases the water electrical conductivity in both tanks. Thus, since the electrical dropdown gets lower in the tanks, the electrical difference applied between both sides of the sample is increasing. The electrical intensity, resulting from ionic transport in the liquid phase, is given in Fig. 3(b). A slight decrease is generally observed in early times. This corresponds to the establishment of the diffusive layer around the carbon electrodes.

Using Eq. (1), the electro-osmotic permeability k_E is calculated at each time step (Fig. 4). Except for the early times ($t < 1000$ s), the electro-osmotic permeability measured is fairly constant and can be approximated by $k_E = 1.52 \times 10^{-9}$ m^2 s^{-1} V^{-1}. This result validates the ability of this experimental procedure to determine the electro-osmotic permeability in gel. This procedure has been repeated by applying increasing electrical potential difference 10, 20 and 30 V on different gel samples. All the results are plotted in Fig. 5. On can notes that the water velocity is a superficial velocity, since it is the flow rate divided by the sample cross-area. The electrical gradient corresponds to the electrical potential difference measured between platinum electrodes divided by the sample thickness. By averaging all the experimental measures, the resulting electro-osmotic permeability of Agar-Agar gel is

$$k_E = 1.29 \times 10^{-9} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1} \tag{2}$$

The discrepancies observed between results are partly attributed to the differences of gel characteristics between samples. Indeed, the physical properties of Agar-Agar gel are very sensitive to the gelification process (temperature, heating time, cooling velocity, . . .) [14], and the elaboration repeatability can hardly be achieved.
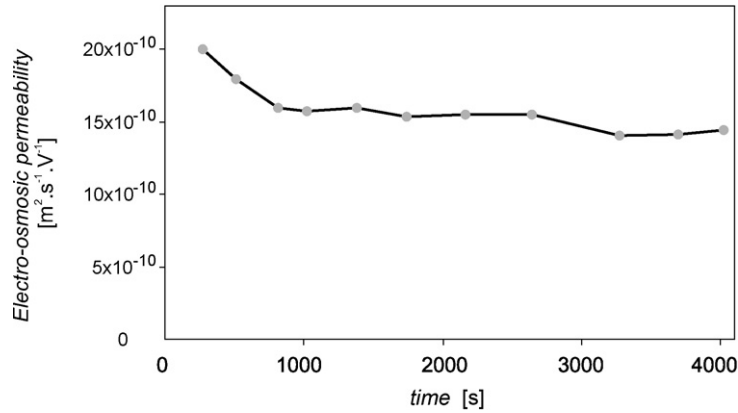
Fig. 4. Experimental results with a 26 mm thick sample submitted to a 10 V electrical potential difference: electro-osmosis permeability calculated using Eq. (1).
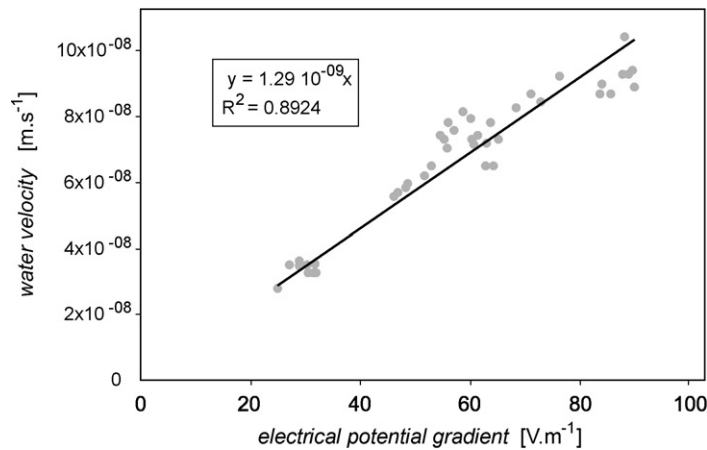

Fig. 5. Synthesis of all experimental results: water velocity through the gel samples versus the electrical potential gradient inside the samples. The equation of the trend line is given with its correlation factor.

As noted in the introduction, experimental values of the electro-osmotic conductivity is between 1×10^{-9} to 1×10^{-8} m^2 V^{-1} s^{-1} for a broad range of soils, from clay to sand [2,8]. The electro-osmotic conductivity of Agar-Agar gel, k_E (Eq. (2)), also lies in this range, even if this material does not share any micro-structural characteristics with soils. It should be recalled that the liquid phase saturating the gel is distilled water, i.e., the only ionic solute results from the water dissociation ([OH$^-$] = [H$^+$] = 10^{-7} mol l^{-1}). It seems that this range of values would have an universal meaning which does not depend on the kind of porous media, the micro-structural geometry or the ionic concentration of the solution.

Based on the Helmholtz–Smoluchowski theory [15], the zeta-potential, ζ, can be deduced from the electro-osmotic permeability according to

$$\zeta = -\frac{\mu \tau^2}{\phi \varepsilon} k_E \tag{3}$$

where $\mu = 0.89 \times 10^{-3}$ kg m^{-1} s^{-1} is the dynamic viscosity of water, $\tau = 1.3$ is the tortuosity estimated from Lakatos et al., 2004 [16], $\phi = 0.96$ is the porosity, $\varepsilon = 6.90 \times 10^{-10}$ F m^{-1} is the permittivity of water. In the case of Agar-Agar gel, this leads to $\zeta = -2.93 \times 10^{-3}$ V, which is about one order lower than the values measured with soils.

5. Conclusion

In food- and bio-engineering research, Agar-Agar gel is commonly used as a reference material to model the swelling/shrinking behaviour induced by hydraulic, electric or osmotic stresses. An experimental investigation dealing with the electro-osmotic characterization of Agar-Agar gel has been presented. The electro-osmotic phenomenon is described by a linear relation, widely used in geotechnical applications, which defines the electro-osmotic permeability. The experimental results show that the electro-osmotic permeability of Agar-Agar gel lies in the limited range usually observed on a large panel of soils, even if the micro-structural characteristics are really different.

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