

Mechanoelectric effects in ionic gels

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Abstract. – Certain fluorinated ion-exchange membranes, when swollen and suitably plated by conducting electrodes, display a spontaneous curvature increasing with the applied electric field $E^{(1)}$. There is also an inverse effect, where an imposed curvature induces an electric field (in open circuit conditions). We present here a compact description of these effects in the linear regime, and in static conditions: this is based on linear irreversible thermodynamics, with two driving forces (E and a water pressure gradient ∇p) and two fluxes (electric current and water current). We also give some qualitative estimates of the three Onsager coefficients which come into play.

Introduction. – Soft, ionic, gels can be distorted by electric fields. This was found long ago on swollen PVA fibers by Hamden *et al.* [1]. In a second step, Tanaka and coworkers [2] used a (partly ionised) polyacrylamide network, swollen by a solvent mixture (water + acetone) which was chosen to be nearly a θ solvent of the chains: they can then commute abruptly from a swollen form to a collapsed form. A third generation of experiments was carried out by Shiga and Kurauchi, who monitored the ambient pH and used electrodes at a distance from the gel [3]. The classical interpretation of these effects [4] is based on ionic currents, creating some local ion exchanges which, in turn, modify the osmotic pressure in the gel.

These very soft gels, however, suffer from certain defects: they give large deformations, but they in turn can induce certain microfractures, and give systems with a very short lifetime. It is of interest to go to more compact systems, which are automatically more robust. In particular, over the last five year, it has been found that certain fluorocarbon networks (carrying a sulfonate function together with a counterion such as Na^+ , and swollen by water) show spectacular deformations under electric fields of order 10 volts/cm [5–7].

An essential trick, required to reach an efficient system, is based on the use of highly divided electrodes (made of platinum, palladium, graphite, conducting polymers), which allow for a stable operation over a very large number of cycles [8]. A global review of the present state of the art is available [9].

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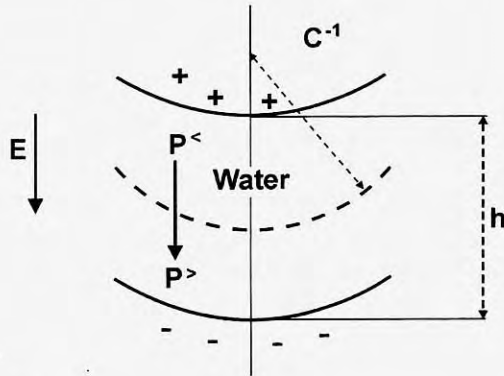


Fig. 1

Fig. 1 – Principle of the “inflation model” after ref. [5]. Under the field E , a water flux (downwards) is entrained by the moving ions (Na^+). This swells the bottom part of the strip, and deswells the top part: the strip bends.

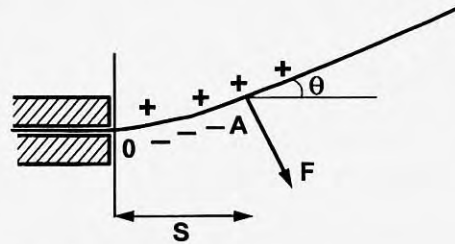


Fig. 2

Fig. 2 – Macroscopic features with a field E favoring positive deflections θ , and a force F , favoring negative deflections. The active part of the strip extends from 0 to A . (It is assumed that no electric fields leak out beyond A).

The most plausible mode of action is slightly different from the osmotic effect, and is expected to be the following [10]: under the field E , the Na^+ ions drift, and they carry with them a certain number of water molecules. When these molecules pile up near the cathode, they create a local overpressure which tends to deform the membrane (a simplified geometry is shown in fig. 1). A thin membrane, which was originally flat, then tends to acquire a certain spontaneous curvature $C(E)$. The role of the entrained water is manifest if we compare $\text{Na}^{(+)}$ and $\text{Li}^{(+)}$, which would be very similar from the point of view of osmotic pressures, and which give very different amplitudes [9].

Detailed transport equations, aiming at a complete description of this effect, are quoted, for instance, in ref. [9]. But they are rather complex, and it is difficult to extract a simple message from them. Our aim in the present paper is more modest. We want to show the basic principles of the direct effect and of the inverse effect in very compact terms. We also limit our discussion to *static* fields E , and we ignore the depletion effects of ref. [4]: the $\text{Na}^{(+)}$ ions are assumed to be present in all the sample⁽¹⁾.

Fluxes and forces. – 1) We are interested in two forms of transport: charge transport (with a current density J normal to the membrane) and solvent transport (with a flux Q). The conjugate forces are the electric field E and the mechanical force $-\nabla p = -\partial p/\partial z$, where p is the (scalar) water pressure in the network. The standard Onsager relations for such a system have the form [10]

$$J = \sigma E - L_{12} \nabla p, \quad (1)$$

$$Q = L_{21} E - K \nabla p. \quad (2)$$

⁽¹⁾At low voltages, an ideal Pt electrode should not produce any current. Some parasitic Faradaic processes occur near the electrodes, and allow the current to go through. But in most of the cell, we do use the “native” ions (here: Na^+).

Here, σ is the membrane conductance, K is the Darcy permeability and $L_{12} = L_{21} = L$ is a cross coefficient discussed in the fifth section.

2) When we measure the *direct effect*, we work (ideally) with electrodes which are impermeable to water, and thus we have $Q = 0$. This gives

$$\nabla p = \frac{L}{K} E. \quad (3)$$

And this ∇p will, in turn, induce a curvature C proportional to ∇p . (This relation will be discussed in the next section).

3) When we study the *inverse effect*, we apply a bending torque Γ to the membrane, and we impose two conditions:

- a) no electric work is produced ($J = 0$).
- b) the strip stays flat.

Then the water pressure gradient ∇p turns out to be proportional to Γ : this is discussed in the third section. The condition $J = 0$ gives, from eq. (1),

$$E = \frac{L}{\sigma} \nabla p \quad (4)$$

and E is thus proportional to Γ .

Curvatures, torques and water pressure gradients. -

Passive strips (fig. 2). - A normal force F (per unit width of the strip) is applied at the free end of the strip, and generates a torque (per unit width) $\Gamma = Fs$, where s is the strip length. The result is a tilt angle θ and a curvature $C = \theta/s$. The energy U (per unit width) has the form

$$U = \frac{1}{2} BC^2 s + \Gamma \theta; \quad (5)$$

B is the bending constant of the strip [11],

$$B = \frac{Yh^3}{12(1 - \sigma_p^2)}, \quad (6)$$

where h is the strip thickness, Y the Young modulus and σ_p the Poisson ratio. Optimising eq. (5) with respect to θ gives a curvature

$$C = -\Gamma/B. \quad (7)$$

Active strip under a field E , in zero torque. - At a distance z from the midplane of the strip, the deformations are of order [7] $\varepsilon = -Cz$ (see fig. 2). The resulting stresses σ are of order $Y\varepsilon$, and the water pressure, which balances them, is comparable:

$$p \cong Y\varepsilon. \quad (8)$$

Thus the pressure gradient is of the form

$$\nabla p = \frac{\partial p}{\partial z} = -kYC. \quad (9)$$

An elastic calculation summarized in the appendix, gives the coefficient k in terms of the Poisson ratio σ_p :

$$k^{-1} = (1 + \sigma_p)(1 - 2\sigma_p). \quad (10)$$

The factor $1 - 2\sigma_p$ is significant: if we had an ideal rubber, with zero bulk compressibility ($\sigma_p = 1/2$) the pressure would induce no curvature.

Fields and torques acting together. – Here, we must add the two contributions to C , described by eqs. (6) and (9). The result is

$$-C = \frac{\nabla p}{kY} + \frac{\Gamma}{B}. \quad (11)$$

We can now couple this mechanical equation with the Onsager relations.

Summary of effects. –

Direct. – We apply an electric field E and a mechanical torque Γ (fig. 2). We choose E so that the effects of E and Γ on the curvature compensate: the sample stays flat ($C = 0$). Then eqs. (3) and (11) give

$$\Gamma = \frac{B}{kY} \nabla p = \frac{1}{12} \frac{1 - 2\sigma_p}{1 - \sigma_p} \frac{Lh^3}{K} E. \quad (12)$$

Inverse. – We now impose a finite water flux Q , but 0 electric current ($J = 0$) and 0 curvature $C = 0$. There will be a certain field E , derived from eq. (4). To maintain $C = 0$, we need a certain torque Γ derived from eq. (11). The relation Γ and E is

$$E = \frac{L}{\sigma} \nabla p = \frac{12(1 - \sigma_p)}{1 - 2\sigma_p} \frac{L}{\sigma h^3} \Gamma. \quad (13)$$

The ratio of the two coefficients is

$$\rho = \left(\frac{\Gamma}{E} \right)_{\text{direct}} / \left(\frac{\Gamma}{E} \right)_{\text{inverse}} = \frac{L^2}{\sigma K}. \quad (14)$$

It is automatically smaller than unity (to insure that the entropy source is positive [6]). The order of magnitude of ρ is discussed in the next section.

The parameter ρ also comes into play in the discussion of the electrical conductance. The conductance σ of eq. (1) is the conductance *at constant water pressure* ($\nabla p = 0$). But if we measure the conductance at zero water flux, we find another value:

$$\tilde{\sigma} = \sigma - \frac{L^2}{K} = \sigma(1 - \rho). \quad (15)$$

Orders of magnitude. – Let us now make a very rough estimate of the various coefficients involved.

1) For the conductivity σ , we write

$$\sigma = \frac{ne^2}{\zeta}, \quad (16)$$

where n is the number of mobile counterions per unit volume, e is the unit charge, and ζ a friction coefficient. In a simple Stokes sphere model, we put $\zeta = \eta a$, where $a/6\pi$ is the equivalent hydrodynamic radius of the ion, and η is the water viscosity.

2) The Darcy permeability can be written as

$$K = \phi \frac{d^2}{\eta}, \quad (17)$$

where ϕ is the volume fraction of water, and d is an effective pore size.

3) The coupled coefficients L can be estimated from eq. (2) in situations from $\nabla p = 0$. The standard discussion on L is based on macroscopic systems, with double layers near the solid surface: each mobile counterion inside the double layer transmits the force eE : this creates a water current dependent on the double layer thickness. But in our system, the pores are very small, and these considerations do not hold. We shall simply assume that each ion carries with itself an overall hydrodynamic volume w due to some hydration process. This is similar in spirit to the model introduced independently by the Japanese group of ref. [7]. Then, the volume current Q is

$$Q = LE = \frac{neE}{\zeta} w \quad (18)$$

and this fixes L . Typical estimates based on this value (with $E = 0.1$ V/cm, $d = 1$ mm, $w \sim 1$ water molecule, and weak swelling: 1 water/SO₃⁻) give a curvature $C \sim 1$ cm⁻¹, which is plausible.

4) From these estimates, we derive immediately the quality ratio ρ of eq. (14): for $\phi \sim 1$, this is

$$\rho = \frac{nw^2}{ad^2}. \quad (19)$$

We see that we need: a large n (many ions); a large entrainment volume w ; and pores which are rather small (small d).

All this discussion is very primitive however, for a number of reasons: a) we ignored all electrode effects, and this is especially weak for a system which contains finely divided conducting particles; b) we ignored the osmotic pressure contributions analysed in ref. [4]. It may be, in fact, that they can be incorporated (by a redefinition of p) into the formulation of the second section.

On the whole, the "inflation model" (where water swells the gel and is driven by the moving ions towards the cathode) seems to provide a plausible description of the effects —*and may also be of interest for some other ionized gels*. But we need detailed comparisons between our predictions of the fourth section and measurements of both direct and inverse effects.

Appendix: Coupling between pressure and curvature. — The starting point is the structure of the strains in a bent elastic plate [11]:

$$e_{xx} = -\frac{z}{R}, \quad (20)$$

where $R \equiv C^{-1}$. Here, z is measured from the midplane,

$$e_{zz} = \frac{\sigma_p}{1 - \sigma_p} \frac{z}{R} + \frac{(1 + \sigma_p)(1 - 2\sigma_p)}{Y(1 - \sigma_p)} p. \quad (21)$$

All other components vanish.

The inplane stress is

$$\sigma_{xx} = -\frac{Y}{1 - \sigma_p^2} \frac{z}{R} + \frac{\sigma_p}{1 - \sigma_p} p. \quad (22)$$

This must satisfy the equilibrium condition

$$\frac{\partial}{\partial x} (\sigma_{xx} - p) = 0, \quad (23)$$

giving

$$-\frac{Y}{1 - \sigma_p^2} \frac{z}{R} + \frac{1 - 2\sigma_p}{1 - \sigma_p} (p - p_0) = 0, \quad (24)$$

where p_0 is the pressure at the midplane. Thus $p - p_0 = z \partial p / \partial z$, and we reach eq. (10).

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