Saturated porous medium strain under osmotic actions

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ABSTRACT: This paper deals with an experimental and theoretical study of a porous medium strain during the transfers of a solution, which is composed of one solvent and only one solute. The porous medium is immersed into the same solution at different concentration. Resulting from concentration gradients, solvent and solute fluxes are created in opposite directions. Under some conditions relatives, for example, to the skeleton texture or to the solute molecule size, this mass transport can generate strains. We present a thermoporoelastic model taking into account the solvent / solute transport and the stresses / strains in a saturated porous medium. The porous medium is assumed to be isotropic, elastic and saturated with an ideal solution. We pay particular attention to the determination of the various parameters of the model. In the isothermal case, we give analytical relations that express the three most specific coefficients of this study.

INTRODUCTION

When a deformable porous medium saturated by an aqueous solution is placed in a solution at different concentration (but of the same composition as the saturating solution), the medium is dehydrated and charged in solute or on the contrary becomes soaked with water and discharged of solute: It is the osmotic dehydration or hydration phenomenon. This communication is concerned by the strain of a saturated porous medium subjected to an osmotic pressure. One of the industrial applications consists in making some molecules (agents of texture, conservatives, tasteful booster cushions, …) penetrate into the medium (fruits, meats, fishes, …) by reducing the moisture content (Raoult-Wack et al. 1992).

In the case of biological media and gels, osmotic dehydration or hydration comes along with important strains. These strains are related to the kind of porosity in the medium and to the size of the solute molecules. Besides, a high concentration gradient amplifies this phenomenon. The example of a spherical sample of agar gel, about 40 mm size, initially saturated with pure water, is illustrated in Figure 1. The sample is soaked into an aqueous solution at different polyethylene glycol concentrations, from 30% to 60%. The diameter is observed as a function of time.

This figure shows clearly that the diameter decreases when concentration increases. Other measurements show that the medium diameter depends also on the solute molecule size as illustrated in Figure 2. It presents a more significant decrease in case of larger molecules. These two results show the osmotic phenomenon influence on the strain of a porous medium.

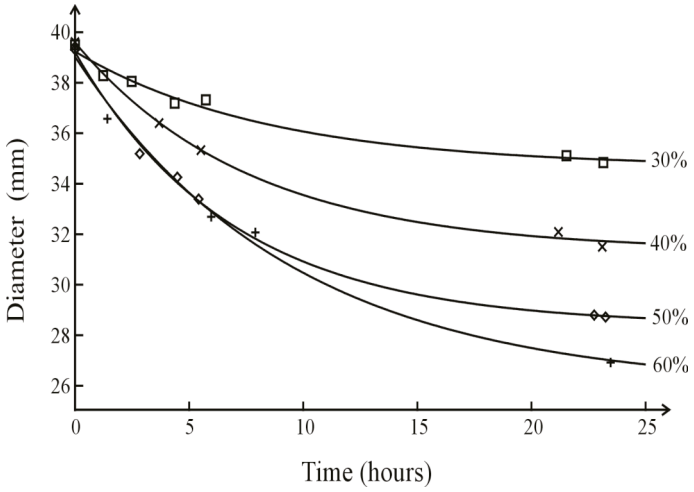

Figure 1. Kinetic of the agar gel diameter decrease for different concentrations of polyethylene glycol.

The approach used gives an extension of the models established by Coussy (1991) and Mrani (1993). This last model uses the same material, but doesn't take the solute penetration into account, which doesn't allow reproducing the experimental results presented above. Another method consists in expressing for each phase the relations of Gibbs, Euler and Gibbs-Duhem (Sicard & Mathieu 1998). However, this method does not allow us to relate the mass transport to the strains.

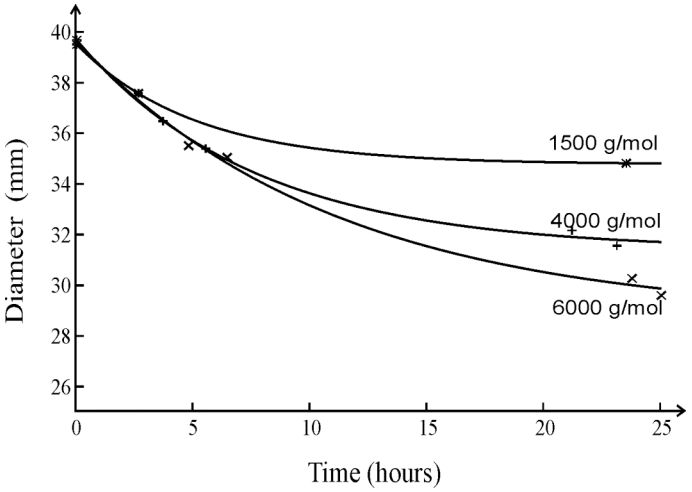

Figure 2. Kinetic of the agar gel diameter decrease for different size of solute molecules (polyethylene glycol).

1 DESCRIPTION OF THE SYSTEM

We consider a porous medium saturated by a solution (noted ℓ). This solution contains a solute (noted *i*) and a solvent (noted *e*) that corresponds to the principal constituent in the liquid phase. The skeleton is deformable and has an elastic behavior. The solid phase (noted *s*) as well as the solution is supposed to be incompressible.

The system state is described using the following variables: the temperature T, the strain linear tensor of the skeleton ε_{kj}, the solvent content $w_e=m_e/m_s$, and the number of moles of the solute n_i by mass unit of solid.

The medium can exchange fluid constituents (solvent and/or solute) with the outside. Solid phase is supposed to be inert. We are interested in the evolution of the medium resulting from an imbalance due to a solute concentration difference between the inside and the outside of the medium.

2 BALANCE EQUATIONS

In the following developments, kinematics and strains are defined by referring to the skeleton.

2.1 *Mass balance equations*

In a volume Ω, the mass of the constituent α is given by:

$$m_\alpha = \int_\Omega \rho_\alpha d\Omega \tag{1}$$

where ρ_α is the apparent bulk mass density of constituent α ($\alpha = s$, e or i).

According to our assumptions, the material derivative (Coussy 1991) of the masses of solid, solvent and solute constituents equals zero. The local mass balance equations are:

$$\frac{\mathrm{d}\rho_s}{\mathrm{d}t} + \rho_s v^k_{s,k} = 0 \tag{2}$$

$$\frac{\mathrm{d}\rho_e}{\mathrm{d}t} + \rho_e v^k_{s,k} + \left(\frac{\rho_e}{\rho_\ell} J^k_\ell\right)_{,k} + \Im^k_{e,k} = 0 \tag{3}$$

$$\frac{\mathrm{d}\rho_i}{\mathrm{d}t} + \rho_i v^k_{s,k} + \left(\frac{\rho_i}{\rho_\ell} J^k_\ell\right)_{,k} + \Im^k_{i,k} = 0 \tag{4}$$

where v_s = velocity of the solid, J_ℓ = filtration flux of the liquid phase through the skeleton, $\Im_e$ and $\Im_i$ are the diffusive fluxes respectively of the solvent and of the solute in the liquid phase. The mass liquid balance is obtained by adding Equations 3 and 4. The balance of total mass is obtained by adding equations 2 through 4.

2.2 *Momentum balance equation*

Using the same development, the momentum conservation principle allows one to derive the following balance equation (Mrani et al. 1995) :

$$\begin{aligned}\sigma_{kj,j} + \rho F^k = \rho\frac{\mathrm{d}v^k_s}{\mathrm{d}t} + \frac{\mathrm{d}J^k_\ell}{\mathrm{d}t} + J^k_\ell v^j_{s,j} + J^j_\ell v^k_{s,j} \\ + \left(\frac{J^k_\ell J^j_\ell}{\rho_\ell}\right)_{,j} + \left(\frac{\Im^k_e \Im^j_e}{\rho_e}\right)_{,j} + \left(\frac{\Im^k_i \Im^j_i}{\rho_i}\right)_{,j}\end{aligned} \tag{5}$$

where ρ is the total bulk mass density given by:

$$\rho = \rho_s + \rho_\ell = \rho_s + \rho_e + \rho_i \tag{6}$$

ρF^k is the forces of volume acting in Ω. σ_{kj} is the total stress tensor.

2.3 *Total energy Balance equation*

The total energy balance is obtained by applying the first thermodynamics principle to the material system contained in a volume element at a time t.

$$\left[J_\ell^k(\gamma_\ell^k - F^k) + \Im_e^k(\gamma_e^k - \gamma_i^k)\right] + \sigma_{kj} v_{s,j}^k + q_{,k}^k$$
$$+ \frac{\mathrm{d}(\rho \cdot e)}{\mathrm{d}t} - (\rho \cdot e) v_{s,j}^k + \left[\left(\frac{\rho_e}{\rho_\ell} J_\ell^k + \Im_e^k\right) h_e\right]_{,k} \quad (7)$$
$$+ \left[\left(\frac{\rho_i}{\rho_\ell} J_\ell^k + \Im_i^k\right) h_i\right]_{,k} = 0$$

where e designates internal energy, γ_ℓ, γ_e and γ_i are respectively phenomenological accelerations of the liquid phase, the solvent and the solute. h_e and h_i are the mass enthalpies of the solvent and the solute and q is the heat flux.

2.4 *Expression of the Entropy relation*

2.4.1 *Gibbs relation*

With the chosen state variables, Gibbs relation is written in the following form:

$$T\mathrm{d}s' = \mathrm{d}e' - \frac{\sigma_{kj}}{\rho_s}\mathrm{d}\varepsilon_{kj} - m_s\mu_e\mathrm{d}w_e - M_i\mu_i\mathrm{d}n_i \quad (8)$$

where *s'* and *e'* are respectively the entropy and the specific internal energy regarding to the mass unit of solid. μ_e and μ_i are chemical mass potential of the solvent and the solute. M_i is the molar mass of the solute ($M_i = m_i/n_i$).

2.4.2 *Source of entropy and phenomenological relations*

By introducing the mass and energy balances into the Gibbs Equation 8, we obtain the entropy balance equation in the following terms:

$$\rho_s \frac{\mathrm{d}s'}{\mathrm{d}t} + \frac{J_{T,k}^k}{T} = \chi_T^k \cdot J_T^k + \chi_\ell^k \cdot J_\ell^k + \chi_e^k \cdot \Im_e^k + \chi_i^k \cdot \Im_i^k \quad (9)$$

where:

$$J_T^k = q^k + T\left(\frac{\rho_e}{\rho_\ell} J_\ell^k + \Im_e^k\right) s_e + T\left(\frac{\rho_i}{\rho_\ell} J_\ell^k + \Im_i^k\right) s_i \quad (10)$$

$$\chi_T^k = \left(\frac{1}{T}\right)_{,k} \quad (11)$$

$$\chi_\ell^k = -\frac{1}{T}\left((\gamma_\ell^k - F^k) + \frac{\rho_e}{\rho_\ell}\mu_{e,k} + \frac{\rho_i}{\rho_\ell}\mu_{i,k}\right) \quad (12)$$

$$\chi_e^k = -\frac{1}{T}(\gamma_e^k - \mu_{e,k}) \quad (13)$$

$$\chi_i^k = -\frac{1}{T}(\gamma_i^k - \mu_{i,k}) \quad (14)$$

where s_e and s_i are the specific entropies of the solvent and solute. Near equilibrium, the linear TIP (Thermodynamics of Irreversible Processes) allows one to deduce the phenomenological relations. These relations express in a linear way the thermodynamic forces χ as some functions of the associated fluxes J and $\Im$. Equation 12 leads to the generalized Darcy's law and Equation 13 gives the solvent transport law that makes appear the osmotic pressure (Ruiz & Bénet 1998).

3 STATE EQUATIONS

If the variable T, ε, w_e and n_i are sufficient to describe the system state, then we can express free energy as follows:

$$\Phi = \Phi(T, \varepsilon, w_e, n_i) = e' - Ts' \quad (15)$$

The differential of Φ can be written by Gibbs' relation:

$$\mathrm{d}\Phi = -s'\mathrm{d}T + \frac{\sigma_{kj}}{\rho_s}\mathrm{d}\varepsilon_{kj} + m_s\mu_e\mathrm{d}w_e + M_i\mu_i\mathrm{d}n_i \quad (16)$$

Since $\mathrm{d}\Phi$ is a total exact differential, we can extract from it the formal expressions of the following state equations:

$$s' = -\frac{\partial\Phi}{\partial T}; \qquad \sigma_{kj} = \rho_s\frac{\partial\Phi}{\partial\varepsilon_{kj}};$$
$$\mu_e = \frac{1}{m_s}\frac{\partial\Phi}{\partial w_e}; \qquad \mu_i = \frac{1}{M_i}\frac{\partial\Phi}{\partial n_i} \quad (17)$$

By using the method proposed by Coussy (1991), for small perturbations around a reference state noted by a superscript (^{0}), second order limited development of the potential free energy around this state is:

$$\rho_s\Phi = \rho_s\Phi^0 - \rho_s s'^0\Delta T + \sigma_{kj}^0\Delta\varepsilon_{kj} + \rho_s m_s\mu_e^0\Delta w_e$$
$$+ \rho_s M_i\mu_i^0\Delta n_i - \frac{C_\varepsilon}{2T^0}\Delta T^2 + \frac{\lambda}{2}(\Delta\varepsilon_{kk})^2 + \mu\Delta\varepsilon_{kj}\Delta\varepsilon_{kj}$$
$$+ \frac{1}{2}d_w^e\Delta w_e^2 + \frac{1}{2}d_{n_i}^i\Delta n_i^2 - 3K\left[\alpha_T\Delta T + \beta_e\Delta w_e\right]\delta_{kj}\Delta\varepsilon_{kj} \quad (18)$$
$$+ d_T^e\Delta T\Delta w_e + d_T^i\Delta T\Delta n_i + (d_\varepsilon^i)_{kj}\Delta\varepsilon_{kj}\Delta n_i - d_{n_i}^e\Delta w_e\Delta n_i$$

where λ and μ are the Lamé's coefficients; C_ε is the mass heat with constant strain; K is the coefficient of compressibility; α_T is the thermic expansion coefficient. Besides these coefficients, already known in the literature, we find the hygrometric expansion coefficient β_e as well as two coefficients d_w^e and d_T^e which are similar to those introduced notably by Sih et al. (1986) and Mrani et al. (1995) without solute. Finally, three coefficients appear: $d_{n_i}^e$, $d_{n_i}^i$ and $(d_{\mathring{a}}^i)_{kj}$ which are specific in this modeling and re-

lated to the presence of solute. These coefficients are the object of particular developments in the fourth section.

Considering Equation 17, the Equation 18 allows one to establish explicitly the following state relations:

$$\Delta s' = \frac{C_\varepsilon}{T^0 \rho_s}\Delta T + \frac{3K\alpha_T}{\rho_s}\delta_{kj}\Delta\varepsilon_{kj} - \frac{d^e_T}{\rho_s}\Delta w_e - \frac{d^i_T}{\rho_s}\Delta n_i \quad (19)$$

$$\Delta\mu_e = \frac{1}{m_s\rho_s}(d^e_w\Delta w_e - 3K\beta_e\delta_{kj}\Delta\varepsilon_{kj} + d^e_T\Delta T - d^e_{n_i}\Delta n_i) \quad (20)$$

$$\Delta\mu_i = \frac{1}{M_i\rho_s}(d^i_{n_i}\Delta n_i + (d^i_\varepsilon)_{kj}\Delta\varepsilon_{kj} + d^i_T\Delta T - d^e_{n_i}\Delta w_e) \quad (21)$$

$$\Delta\sigma_{kj} = \lambda\Delta\varepsilon_{ii}\delta_{kj} + 2\mu\Delta\varepsilon_{kj} - 3K(\alpha_T\Delta T + \beta_e\Delta w_e)\delta_{kj} + (d^i_\varepsilon)_{kj}\Delta n_i \quad (22)$$

4 DETERMINATION OF THE COEFFICIENTS

The exploitation of Equations 19 through 22 requires the determination of the state coefficients, from experimental measures. Mechanical or thermic coefficients are classic although particular precautions should be taken for their determination in the context of this study. If we only take into account isothermal situations, five coefficients require a specific experimental study: namely d^e_w, β_e, $d^e_{n_i}$, $d^i_{n_i}$ and $(d^i_\sigma)_{kj}$. The first two coefficients should be compared with two coefficients d_w and β introduced by Mrani et al. (1995). Then, we show, using some assumptions, how to reach the three other coefficients less known, namely:

- Coefficients $d^e_{n_i}$ and $d^i_{n_i}$ which express the dependence of solvent / solute chemical potential on solute concentration.
- Coefficient $(d^i_\sigma)_{kj}$, which gives the influence of the solute concentration on stresses.

4.1 *Coefficient* $d^i_{n_i}$

This coefficient results from a solute chemical potential variation according to an infinitesimal variation of the solute mole number in a solid unit mass volume. It is given by the relation:

$$d^i_{n_i} = \tilde{n}_s M_i\left(\frac{\partial\lambda_i}{\partial n_i}\right)_{T,\varepsilon_{kj},w_e} \quad (23)$$

In the case of an ideal solution, mass chemical potential of the solute can be expressed as (Arnaud 1995):

$$\mu_i = \mu_i^+(T) + \frac{RT}{M_i}\ln\frac{n_i}{n_e + n_i} \quad (24)$$

where μ_i^+ is the mass chemical potential of the constituent i in the pure state, and R is the constant of the perfect gases. We can therefore write:

$$\frac{\partial\mu_i}{\partial n_i} = \frac{RTn_e}{M_i n_i(n_e + n_i)} \quad (25)$$

Soustelle (1990) leads to the same expression by using the molar chemical potential $\tilde{\tau}_i = M_i\lambda_i$. Equations 23 and 25 enable us to write:

$$d^i_{n_i}(T,n_i) = \rho_s\frac{RTn_e}{n_i(n_e + n_i)} \quad (26)$$

In the case of a very diluted solution, Equation 26 can be approximated by:

$$d^i_{n_i}(T,n_i) = \rho_s\frac{RT}{n_i} \quad (27)$$

4.2 *Coefficient* $d^e_{n_i}$

This coefficient results from a solvent chemical potential variation according to an infinitesimal variation of the solution mole number in a solid unit mass volume. It is given by the relation:

$$d^e_{n_i} = -\tilde{n}_s m_s\left(\frac{\partial\lambda_e}{\partial n_i}\right)_{T,\varepsilon_{kj}} \quad (28)$$

The Maxwell Relations of symmetry allow writing:

$$\frac{\partial\tilde{\tau}_e}{\partial n_i} = \frac{\partial\tilde{\tau}_i}{\partial n_e} \quad (29)$$

or by using Equation 24:

$$\frac{\partial\mu_e}{\partial n_i} = -\frac{RT}{M_e(n_e + n_i)} \quad (30)$$

and therefore, coefficient $d^e_{n_i}$ is expressed as:

$$d^e_{n_i}(T,w_e,n_i) = \tilde{n}_s m_s\frac{RT}{M_e(n_e + n_i)} \quad (31)$$

or by using the solvent content state variable w_e:

$$d^e_{n_i}(T,w_e,n_i) = \tilde{n}_s m_s\frac{M_e}{M_i}\frac{RT}{(w_e m_s + M_e n_i)} \quad (32)$$

4.3 *Coefficient* $(d_\varepsilon^i)_{kj}$

This coefficient results from a variation of the Cauchy's stresses tensor when the quantity of solute varies at fixed temperature and solvent content. It is given by the relation:

$$(d_\varepsilon^i)_{kj} = \left(\frac{\partial \sigma_{kj}}{\partial n_i}\right)_{T,w_e} \tag{33}$$

If we adopt the decomposition of the stress tensor σ_{kj} in two tensors of average stresses σ_{kj}^s and σ_{kj}^ℓ respectively in the solid phase and liquid phase:

$$\sigma_{kj} = \sigma_{kj}^s + \sigma_{kj}^\ell \tag{34}$$

This decomposition leads to propose the following expression (Coussy 1991):

$$\sigma_{kj} = (1-\phi)\sigma_{kj}^{s*} + \phi\sigma_{kj}^{\ell*} \tag{35}$$

where ϕ is the porosity defined as the ratio of the pore volume to the total volume. The variables with superscript* refer to the microscopic level. Equation 35 suggests that on a tiny element of surface, the stress vector is associated to the actions of both solid and solution according to the volume fraction occupied by each phase. In case of a saturated medium, the assumption of a non-sticky solution (i.e. the average stress tensor of the liquid σ_{kj}^ℓ reduces to a spherical tensor characterized by the phenomenological pressure $P_\ell = \phi P_\ell^*$ where P_ℓ^* is the pore pressure) leads to the following decomposition of the stress tensor:

$$\sigma_{kj} = (1-\phi)\sigma_{kj}^{s*} - \phi P_\ell^* \delta_{kj} \tag{36}$$

Assuming that the solute does not penetrate into the solid phase and does not precipitate. This allows one to reduce the Equation 33 to:

$$(d_\varepsilon^i)_{kj} = \left(-\phi\frac{\partial P_\ell^*}{\partial n_i}\delta_{kj}\right)_{T,w_e} \tag{37}$$

Equation 37 shows that this coefficient is reduced to a scalar. The same conclusion can be deduced from the isotropy assumption. Indeed, this condition imposes that:

$$(d_\varepsilon^i)_{11} = (d_\varepsilon^i)_{22} = (d_\varepsilon^i)_{33} = d_\varepsilon^i \tag{38}$$

A sign change of variations $\Delta\varepsilon_{12}$, $\Delta\varepsilon_{13}$ and $\Delta\varepsilon_{23}$ in the state Equation 21 can not modify the variation of the mass chemical potential of the solution, therefore:

$$(d_\varepsilon^i)_{12} = (d_\varepsilon^i)_{13} = (d_\varepsilon^i)_{23} = 0 \tag{39}$$

In the case of a porous medium saturated by a solution, the mass chemical potential of the solvent can be written (Ruiz & Bénet 1998):

$$\mu_e = \mu_e^+(T) + \frac{1}{\rho_e^*}(P_\ell^* - \pi) \tag{40}$$

where $\mu_e^+(T)$ depends only on the temperature, π = the osmotic pressure given by the Van't Hoff law:

$$\pi = RT\frac{n_i}{V_\ell} \tag{41}$$

By using Equations 30, 40 and 41, we find:

$$(d_\varepsilon^i)_{kj} = \frac{RT}{V}\left(1 - \frac{n_e}{n_e + n_i}\right)\delta_{kj} \tag{42}$$

In the case of a diluted solution ($n_i << n_e$), this coefficient is negligible, and the corresponding terms in Equations 21 and 22 can be neglected.

Within the framework of adopted assumptions, this result shows that the chemical potential of the solute *i* is not affected by the deformation of the solid (Equation 21). By taking this coefficient equal to zero in the Equation 22, we notice that the influence of the mass transport on the variation of the stress tensor is due essentially to the variation of the solvent content through the hygrometric expansion coefficient β_e.

Let us note that the solute transport participates in an implicit way. The law of solvent transfer (Ruiz & Bénet 1998) depends on the osmotic pressure gradient, which is directly related to the gradient of solute concentration.

CONCLUSION

The clear influence, of the solute molecules size and concentration on the osmotic dehydration of a deformable porous medium, was shown. We proposed a modeling of the phenomenon by privileging the solid phase. The balance equations and the phenomenological relations were thus established. A second order development of the free energy potential has allowed us to derive the state equations concerning mass chemical potentials and stresses. These state equations make appear phenomenological coefficients. Some of these coefficients have already been analyzed in the case of a solvent without solute. Others are related to the presence of the solute. Simple analytical expressions allow one to quantify these coefficients. A numerical implementation of this model would enable to emphasize the behavior of deformable porous media under osmotic pressure gradient effects. Applications in gels and in biological media will then be possible.

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