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QUADRIPHASIC MECHANICS OF SWELLING INCOMPRESSIBLE POROUS MEDIA

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Abstract—A chemo-electro-mechanical formulation of quasi-static finite deformation of swelling incompressible porous media is derived from mixture theory. The model consists of an electrically charged porous solid saturated with a monovalent ionic solution. Incompressible and isothermal deformation is assumed. Hydration forces are neglected. The mixture as a whole is assumed locally electroneutral. Four phases following different kinematic paths are defined: solid, fluid, anions and cations. Balance laws are derived for each phase and for the mixture as a whole. A Lagrangian form of the second law of thermodynamics is derived for incompressible porous media and is used to derive the constitutive relationships of the medium. It is shown that the theory is consistent with Biot's theory for the limiting case without ionic effects and with Staverman's results for the limiting case without deformation. © 1997 Elsevier Science Ltd.

1. INTRODUCTION

Biological, mineral and synthetic porous media often exhibit swelling or shrinking when in contact with changing salt concentrations. This phenomenon, observed in clays, shales, cartilage and gels, is caused by a combination of electrostatic forces and hydration forces [1, 2]. Four phases are involved in the swelling mechanics: a solid, a fluid, anions and cations. Lai *et al.* [2] developed a triphasic theory for soft hydrated tissue and applied the theory to cartilage while neglecting electrical flux, geometric non-linearities and hydration forces. They verified the theory for one-dimensional equilibrium results. Snijders *et al.* [3] developed a family of finite elements for two-dimensional, three-dimensional and axisymmetric analysis of finite deformation of triphasic media. In addition they performed one-dimensional transient experiments on swelling and consolidation of intervertebral disc tissue [4]. As electrical effects like electro-osmosis and streaming currents are experimentally well-established in these media [5], this paper focuses on including these effects. Hydration forces are not considered in this paper. Achanta *et al.* [6], and Achanta and Cushman [7], have developed a hybrid mixture model including hydration forces. As hydration forces are often the dominant swelling factor in mineral porous media [1], Achanta's model should be preferred for these applications. In this paper, we present a derivation of a quadruphase theory of swelling incompressible porous media. In order to simplify the mathematics as much as possible, a Lagrangian form of the entropy inequality will be derived, which leads to equations consistent with Biot's porous media theories in a more straightforward way than the more familiar Eulerian approach of Bowen [8]. The incompressibility and electroneutrality conditions are introduced by means of two Lagrange multipliers; the latter is physically interpreted as an electrical potential, the former as a pressure.

2. DONNAN OSMOSIS

Many biological tissues and gels exhibit the phenomenon of swelling. This phenomenon is often caused by electric charges fixed to the porous solid, counteracted by corresponding

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charges in the fluid. When such a medium is in contact with a monovalent salt solution, the diffusion of salt ions and flow of fluid take place between the medium and the salt solution until equilibrium is reached:

$$\mu^+ = \bar{\mu}^+ \quad (1)$$

$$\mu^- = \bar{\mu}^- \quad (2)$$

$$\mu^f = \bar{\mu}^f. \quad (3)$$

Here, μ^+ is the electrochemical potential of the cations, μ^- is the electrochemical potential of the anions and μ^f the chemical potential of the fluid in the medium. The corresponding overlined symbols refer to chemical potentials in the outer solution. Standard expressions for (electro) chemical potentials are found in the literature [9]. If we assume incompressibility for each constituent, i.e. same partial molar volumes in either solution, we find:

$$\mu^+ = \mu_0^+ + \frac{1}{\bar{V}^+} (RT \ln a^+ + F \xi) \quad (4)$$

$$\mu^- = \mu_0^- + \frac{1}{\bar{V}^-} (RT \ln a^- - F \xi) \quad (5)$$

$$\mu^f = \mu_0^f + p + \frac{RT}{\bar{V}^f} \ln a^f \quad (6)$$

in which μ_0^β are reference values, $\bar{V}^\beta$ partial molar volumes, a^β activities, p the fluid pressure, T absolute temperature, R universal gas constant, F Faraday's constant and ξ the electrical potential. All of these (electro)chemical potentials are measured here per unit volume constituent. The combination of equations (1) and (2) leads to

$$a^- a^+ = \bar{a}^+ \bar{a}^- \quad (7)$$

$$\xi - \bar{\xi} = \frac{RT}{2F} \ln \frac{a^- \bar{a}^+}{a^+ \bar{a}^-} \quad (8)$$

where $\xi - \bar{\xi}$ is the Donnan potential between the inner and outer solution. If we define c^{fc} as the fixed charge density per unit fluid volume of the inner solution, taken positive for positive charges and negative for negative charges, we can write the electroneutrality conditions as

$$c^- = c^+ + c^{fc} \quad (9)$$

$$\bar{c}^- = \bar{c}^+ = \bar{c} \quad (10)$$

where c^+ and c^- are the cationic and anionic concentrations per unit fluid volume in the inner solution, while the corresponding overlined symbols pertain to the outer solution. From the previous equations we derive the Donnan equilibrium concentration of the ions:

$$2c^+ = -c^{fc} + \sqrt{(c^{fc})^2 + 4f^2 \bar{c}^2} \quad (11)$$

$$2c^- = c^{fc} + \sqrt{(c^{fc})^2 + 4f^2 \bar{c}^2} \quad (12)$$

with

$$f^2 = \frac{\bar{f}^+ \bar{f}^-}{f^+ f^-} \quad (13)$$

and $f^\beta = \frac{a^\beta}{c^\beta}$, $\beta = +, -$ the activity coefficient of component β . Equations (11) and (12) show that the cationic concentration jumps to a higher and the anionic concentration to a lower value when entering the porous medium. These concentration jumps are responsible for the attraction of water into the porous medium during swelling and for the associated osmotic pressure π . Using equation (6) one can derive Van't Hoff relation from equation (3):

$$\pi = p - \bar{p} = RT[\phi^f(c^+ + c^-) - 2\bar{\phi}^f\bar{c}] \quad (14)$$

provided that the molar fractions of the ions are small compared to the molar fraction of the fluid. ϕ^f and $\bar{\phi}^f$ are the osmotic coefficients:

$$\phi^f = \frac{\partial \ln a^f}{\partial \ln x^f} \quad (15)$$

$$\bar{\phi}^f = \frac{\partial \ln \bar{a}^f}{\partial \ln \bar{x}^f}. \quad (16)$$

$x^f = \frac{c^f}{\sum c^\beta}$ and $\bar{x}^f = \frac{\bar{c}^f}{\sum \bar{c}^\beta}$ are the molar fractions of the fluid in the inner and outer solution. It may be clear from the above considerations that physical phenomena occurring in the porous medium are a combination of mechanical, chemical and electrical effects. The interrelationship between these effects are well-known for membrane processes [10]. The purpose of this paper is to generalise these relationships for porous media subjected to three-dimensional finite deformation. The four phases that we consider in the medium are: solid (superscript s), fluid (superscript f), monovalent anions (superscript $-$) and monovalent cations (superscript $+$). In the next section we derive the equations from mixture theory.

3. THEORY OF SWELLING MEDIA

Assuming all components intrinsically incompressible and excluding mass transfer between phases, the mass balance of each phase is written as:

$$\frac{\partial n^\alpha}{\partial t} + \nabla \cdot (n^\alpha \mathbf{v}^\alpha) = 0, \alpha = s, f, +, - \quad (17)$$

in which n^α is the volume fraction and $\mathbf{v}^\alpha$ the velocity of phase α . As we assume saturation

$$n^s + n^f + n^+ + n^- = 1 \quad (18)$$

and as we neglect the volume fraction of the ions relative to the other volume fractions, summation of the equation (17) yields the mass balance of the mixture:

$$\nabla \cdot \mathbf{v}^s + \nabla \cdot (n^f(\mathbf{v}^f - \mathbf{v}^s)) = 0. \quad (19)$$

At this point it is useful to refer to current descriptors of the mixture, with respect to an initial state of the porous solid. As is usual in continuum mechanics, we define the deformation gradient tensor $\mathbf{F}$ mapping an infinitesimal material line segment in the initial state of the solid onto the corresponding infinitesimal line segment in the current state of the solid. The relative

volume change from the initial to the current state is the determinant of the deformation gradient tensor $J = \det \mathbf{F}$. If we introduce volume fractions

$$N^\alpha = J n^\alpha \quad (20)$$

per unit initial volume, we can rewrite the mass balance equation (17) as follows:

$$\frac{D^s N^\alpha}{D t} + J \nabla \cdot [n^\alpha (\mathbf{v}^\alpha - \mathbf{v}^s)] = 0 \quad (21)$$

when using the identity:

$$\frac{D^s}{D t} J = J \nabla \cdot \mathbf{v}^s. \quad (22)$$

Neglecting body forces and inertia, the momentum balance takes the form

$$\nabla \cdot \boldsymbol{\sigma}^\alpha + \boldsymbol{\pi}^\alpha = \mathbf{0}, \alpha = s, f, +, - \quad (23)$$

which after summation over the four phases, yields

$$\nabla \cdot \boldsymbol{\sigma} = \nabla \cdot \boldsymbol{\sigma}^s + \nabla \cdot \boldsymbol{\sigma}^f + \nabla \cdot \boldsymbol{\sigma}^+ + \nabla \cdot \boldsymbol{\sigma}^- = \mathbf{0} \quad (24)$$

if use is made of the balance condition:

$$\boldsymbol{\pi}^s + \boldsymbol{\pi}^f + \boldsymbol{\pi}^+ + \boldsymbol{\pi}^- = \mathbf{0}. \quad (25)$$

Here $\boldsymbol{\sigma}^\alpha$ is the partial stress tensor of constituent α , $\boldsymbol{\pi}^\alpha$ is the momentum interaction with constituents other than α . Balance of moment of momentum requires that the stress tensor $\boldsymbol{\sigma}$ be symmetric. If no moment of momentum interaction between components occurs, the partial stresses $\boldsymbol{\sigma}^\alpha$ also are symmetric. In this paper we assume all partial stresses to be symmetric. Under isothermal and incompressible conditions, the entropy inequality for a unit volume of mixture reads [8]:

$$\sum_{\alpha=s,f,+, -} \left(-n^\alpha \frac{D^\alpha \Psi^\alpha}{D t} + \boldsymbol{\sigma}^\alpha : D^\alpha - \boldsymbol{\pi}^\alpha \cdot \mathbf{v}^\alpha \right) \geq 0 \quad (26)$$

in which Ψ^α is the Helmholtz free energy of constituent α per unit volume constituent. We introduce the strain energy function

$$W = J \sum_{\alpha=s,f,+, -} n^\alpha \Psi^\alpha = J \sum_{\alpha=s,f,+, -} \psi^\alpha \quad (27)$$

as the Helmholtz free energy of a mixture volume which in the initial state of the solid equals unity. ψ^α is the Helmholtz free energy of constituent α per unit mixture volume. Rewriting the inequality equation (26) for the entropy production per initial mixture volume, i.e. we multiply inequality equation (26) by the relative volume change J , we find:

$$- \frac{D^s}{D t} W + J \boldsymbol{\sigma} : \nabla \mathbf{v}^s + J \nabla \cdot \sum_{\beta=f,+, -} [(\mathbf{v}^\beta - \mathbf{v}^s) \cdot \boldsymbol{\sigma}^\beta - (\mathbf{v}^\beta - \mathbf{v}^s) \psi^\beta] \geq 0. \quad (28)$$

The entropy inequality should hold for an arbitrary state of the mixture, complying with the

balance laws, incompressibility and electroneutrality. The mass balance of the mixture equation (19) is substituted by means of a Lagrange multiplier p :

$$-\frac{D^s}{Dt} W + J \boldsymbol{\sigma}^{\text{eff}} : \nabla \mathbf{v}^s + J \sum_{\beta=f,+, -} [\boldsymbol{\sigma}^\beta + (pn^\beta - \psi^\beta) \mathbf{I}] : \nabla (\mathbf{v}^\beta - \mathbf{v}^s) + J \sum_{\beta=f,+, -} (\mathbf{v}^\beta - \mathbf{v}^s) \cdot (-\nabla \psi^\beta + p \nabla n^\beta + \nabla \cdot \boldsymbol{\sigma}^\beta) \geq 0 \quad (29)$$

in which the effective stress $\boldsymbol{\sigma}^{\text{eff}}$ is defined as

$$\boldsymbol{\sigma}^{\text{eff}} = \boldsymbol{\sigma} + p \mathbf{I}. \quad (30)$$

The electroneutrality condition equation (9) is rewritten in the form:

$$C^- = C^+ + C^{\text{fc}} \quad (31)$$

in which C^β is the current molar concentration per unit initial mixture volume:

$$C^\beta = J n^f c^\beta \beta = +, -, \text{fc}. \quad (32)$$

As the fixed charges are linked to the solid, we know that

$$\frac{D^s C^{\text{fc}}}{Dt} = 0. \quad (33)$$

Differentiation of equation (37) with respect to time yields:

$$\frac{D^s C^-}{Dt} = \frac{D^s C^+}{Dt} \quad (34)$$

or, after substitution of equation (21)

$$\frac{1}{\bar{V}^+} \nabla \cdot [n^+ (\mathbf{v}^+ - \mathbf{v}^s)] = \frac{1}{\bar{V}^-} \nabla \cdot [n^- (\mathbf{v}^- - \mathbf{v}^s)] \quad (35)$$

in which $\bar{V}^\beta$ are the partial molar volumes of the ions. Introducing the restriction equation (35) into inequality equation (29) by means of a Lagrange multiplier λ , yields:

$$-\frac{D^s}{Dt} W + J \boldsymbol{\sigma}^{\text{eff}} : \nabla \mathbf{v}^s + J \sum_{\beta=f,+, -} \left[\boldsymbol{\sigma}^\beta + \left(\left(p + \frac{z^\beta \lambda}{\bar{V}^\beta} \right) n^\beta - \psi^\beta \right) \mathbf{I} \right] : \nabla (\mathbf{v}^\beta - \mathbf{v}^s) + J \sum_{\beta=f,+, -} (\mathbf{v}^\beta - \mathbf{v}^s) \cdot \left[-\nabla \psi^\beta + \left(p + \frac{z^\beta \lambda}{\bar{V}^\beta} \right) \nabla n^\beta + \nabla \cdot \boldsymbol{\sigma}^\beta \right] \geq 0 \quad (36)$$

in which z^β is the valence of constituent β . We choose as independent variables the Green strain $\mathbf{E}$, the Lagrangian form of the volume fractions of the fluid and the ions N^β , and of the relative velocities $\mathbf{v}^{\beta s} = \mathbf{F}^{-1} \cdot (\mathbf{v}^\beta - \mathbf{v}^s)$, $\beta = f, +, -$. We apply the principle of equipresence, i.e. all

dependent variables depend on all independent variables, unless the entropy inequality requires otherwise. We apply the chain rule for time differentiation of W :

$$\left(J \boldsymbol{\sigma}^{\text{eff}} - \mathbf{F} \cdot \frac{\partial W}{\partial \mathbf{E}} \cdot \mathbf{F}^c \right) : \nabla \mathbf{v}^s + \sum_{\beta=f,+, -} \left\{ \frac{\partial W}{\partial \mathbf{v}^{\beta s}} \cdot \frac{D^s}{Dt} \mathbf{v}^{\beta s} + J [\boldsymbol{\sigma}^{\beta} + (\mu^{\beta} n^{\beta} - \psi^{\beta}) \mathbf{I}] : \nabla (\mathbf{v}^{\beta} - \mathbf{v}^s) + J (\mathbf{v}^{\beta} - \mathbf{v}^s) \cdot (-\nabla \psi^{\beta} + \mu^{\beta} \nabla n^{\beta} + \nabla \cdot \boldsymbol{\sigma}^{\beta}) \right\} \geq 0 \quad (37)$$

in which μ^{β} are the electrochemical potentials of fluid and ions:

$$\mu^f = \frac{\partial W}{\partial N^f} + p; \mu^+ = \frac{\partial W}{\partial N^+} + \frac{\lambda}{V^+}; \mu^- = \frac{\partial W}{\partial N^-} - \frac{\lambda}{V^-}. \quad (38)$$

We use the mass balance of the constituents equation (21) to obtain inequality equation (37) from equation (36). Comparison of equation (38) to the classical equations of electrochemistry equations (4)–(6) indicates that the Lagrange multiplier p can be interpreted as the fluid pressure and λ as the electrical potential of the medium multiplied by the constant of Faraday. Assume we make a choice for all field variables appearing in inequality equation (37). For this particular set of choices, we comply with the balance of mass of the constituents equation (21)

by appropriate choices of $\frac{D^s N^{\alpha}}{Dt}$. We comply with the balance of momentum of the constituents equation (23) by appropriate choices of the momentum interaction terms $\boldsymbol{\pi}^{\alpha}$, with the balance of momentum of the mixture equation (24) by an appropriate choice of the solid stress divergence $\nabla \cdot \boldsymbol{\sigma}^s$, with the saturation condition equation (18) by an appropriate choice of the solid volume fraction n^s and with the incompressibility of the constituents by adequate choices of the apparent densities. We comply with the mass balance of the mixture equation (19) (encompassing incompressibility of the mixture) and with the electroneutrality through the use of Lagrange multipliers. Therefore, inequality equation (37) should be true for any value of the state variables. Close inspection of the choice of independent variables and the inequality equation (37), reveals that the first term of equation (37) is linear in the solid velocity gradient $\nabla \mathbf{v}^s$, the second term linear in $\frac{D^s}{Dt} \mathbf{v}^{\beta s}$ and the third term linear in the relative velocity gradients $\nabla (\mathbf{v}^{\beta} - \mathbf{v}^s)$. Therefore, by a standard argument [11], we find:

$$\boldsymbol{\sigma}^{\text{eff}} = \frac{1}{J} \mathbf{F} \cdot \frac{\partial W}{\partial \mathbf{E}} \cdot \mathbf{F}^c \quad (39)$$

$$\frac{\partial W}{\partial \mathbf{v}^{\beta s}} = 0 \quad (40)$$

$$\boldsymbol{\sigma}^{\beta} = (\psi^{\beta} - \mu^{\beta} n^{\beta}) \mathbf{I} \quad (41)$$

leaving as inequality:

$$\sum_{\beta=f,+, -} J (\mathbf{v}^{\beta} - \mathbf{v}^s) \cdot (-\nabla \psi^{\beta} + \mu^{\beta} \nabla n^{\beta} + \nabla \cdot \boldsymbol{\sigma}^{\beta}) \geq 0. \quad (42)$$

Equation (39) indicates that the effective stress of the mixture can be derived from a strain energy function W which represents the free energy of the mixture. Equation (40) shows that the strain energy function cannot depend on the relative velocities. Thus, the effective stress of a quadriphasic medium can be derived from a regular strain energy function, which physically has

the same meaning as in single phase or biphasic media, but which can depend on both strain and ion concentrations in the medium. According to equation (41) the partial stress of the fluid and the ions are scalars. Transforming the relative velocities to their Lagrangian equivalents, we find instead of equation (42):

$$\sum_{\beta=f,+, -} \mathbf{v}^{\beta s} \cdot [-\nabla_0 \psi^\beta + \mu^\beta \nabla_0 n^\beta + \nabla_0 \cdot \boldsymbol{\sigma}^\beta] \geq 0 \quad (43)$$

in which $\nabla_0 = \mathbf{F}^c \cdot \nabla$ is the gradient operator with respect to the initial configuration. If we assume that the system is not too far from equilibrium, we can express the dissipation equation (43) associated with relative flow of fluid and ions as a quadratic function of the relative velocities:

$$-\nabla_0 \psi^\beta + \mu^\beta \nabla_0 n^\beta + \nabla_0 \cdot \boldsymbol{\sigma}^\beta = \sum_{\gamma=f,+, -} \mathbf{B}^{\beta\gamma} \cdot \mathbf{v}^{\gamma s} \quad (44)$$

$\mathbf{B}^{\beta\gamma}$ is a positive definite matrix of frictional tensors. Substituting equation (41) into equations (44) yields Lagrangian forms of the classical equations of irreversible thermodynamics:

$$-n^\beta \nabla_0 \mu^\beta = \sum_{\gamma=f,+, -} \mathbf{B}^{\beta\gamma} \cdot \mathbf{v}^{\gamma s} \quad (45)$$

In many applications it seems reasonable to assume that:

$$\mathbf{B}^{+f} = -\mathbf{B}^{++} \quad (46)$$

$$\mathbf{B}^{-f} = -\mathbf{B}^{--} \quad (47)$$

$$\mathbf{B}^{+-} = \mathbf{O} \quad (48)$$

Physically, this means that friction between ions and between ions and solid is neglected relative to friction between solid and fluid and friction between ions and fluid. Substituting equation (46)–(48) into equation (45), we find:

$$n^f \nabla_0 \mu^f = -\mathbf{B}^{ff} \cdot \mathbf{v}^{fs} + \mathbf{B}^{++} \cdot \mathbf{v}^{+s} + \mathbf{B}^{--} \cdot \mathbf{v}^{-s} \quad (49)$$

$$n^+ \nabla_0 \mu^+ = -\mathbf{B}^{++} \cdot (\mathbf{v}^{+s} - \mathbf{v}^{fs}) \quad (50)$$

$$n^- \nabla_0 \mu^- = -\mathbf{B}^{--} \cdot (\mathbf{v}^{-s} - \mathbf{v}^{fs}) \quad (51)$$

Adding these three equations yields Darcy's law including electrokinetic and osmotic effects:

$$-(\mathbf{B}^{ff} - \mathbf{B}^{++} - \mathbf{B}^{--}) \cdot \mathbf{v}^{fs} = n^f \nabla_0 \mu^f + n^+ \nabla_0 \mu^+ + n^- \nabla_0 \mu^- \quad (52)$$

In agreement with equation (38), we adopt expressions (4)–(6) for the electrochemical potentials. Darcy's equation can be rewritten as:

$$n^f \mathbf{v}^{fs} = -\mathbf{K} \cdot [\nabla_0(p - \pi) + RT(\phi^+ \nabla_0 c^+ + \phi^- \nabla_0 c^-) - Fc^{fc} \nabla_0 \xi] \quad (53)$$

indicating that fluid flow is caused by gradients of pressure, concentration and electrical potential. π is the osmotic pressure given by equation (14). In analogy with equations (15) and (16), the osmotic coefficients are given by:

$$\phi^\beta = \frac{\partial \ln a^\beta}{\partial \ln x^\beta}, \beta = f, +, - \quad (54)$$

in which x^β is the molar fraction of component β . The permeability tensor is

$$\mathbf{K} = (n^f)^2 (\mathbf{B}^{ff} - \mathbf{B}^{++} - \mathbf{B}^{--})^{-1} \quad (55)$$

Substitution of equation (53) into the mass balance equation (19) yields:

$$\nabla \cdot \mathbf{v}^s - \nabla \cdot \mathbf{F} \cdot \mathbf{K} \cdot [\nabla_0(p - \pi) + RT(\phi^+ \nabla_0 c^+ + \phi^- \nabla_0 c^-) - Fc^{fc} \nabla_0 \xi] = 0 \quad (56)$$

The substitution of equation (50) into the mass balance equation of the ions, yields the diffusion equations:

$$n^f \frac{D^f}{Dt} \frac{N^\beta}{N^f} = \nabla \cdot \mathbf{F} \cdot \mathbf{D}^\beta \cdot \nabla_0 \mu^\beta, \beta = +, - \quad (57)$$

in which $\mathbf{D}^\beta = (n^\beta)^2 (\mathbf{B}^{\beta\beta})^{-1}$ are the diffusion tensors of the ions. The momentum balance equation (24), the mass balance equation (56), the diffusion equation (57), the constitutive relationships of the osmotic pressure π equation (14) and of the effective stress equation (39) form a set of partial differential equations. The boundary conditions are given by a no-jump condition of the electrochemical potential of the ions and the fluid across the boundary and the momentum balance of the boundary. The following sections illustrate that from the above equations several well-known physical theories can be derived.

4. DIFFUSION POTENTIAL

The electric flux through the mixture is

$$\mathbf{i} = F \sum_{\gamma=f,+, -} \frac{n^\gamma z^\gamma}{\bar{V}^\gamma} \mathbf{v}^{\gamma s} \quad (58)$$

$\mathbf{i}$ is defined as the current electric flux through a surface of the mixture which initially equalled a unit surface. If use is made of equation (45), we find

$$\mathbf{i} = -F \sum_{\gamma=f,+, -} z^\gamma \sum_{\beta=f,+, -} \mathbf{L}^{\beta\gamma} \cdot \bar{V}^\beta \nabla_0 \mu^\beta \quad (59)$$

in which $\mathbf{L}^{\beta\gamma}$ are the conductances:

$$\mathbf{L}^{\beta\gamma} = \frac{n^\gamma n^\beta (\mathbf{B}^{-1})^{\beta\gamma}}{\bar{V}^\beta \bar{V}^\gamma} \quad (60)$$

$\mathbf{B}^{-1}$ is the inverse of the matrix of tensors $[\mathbf{B}^{\beta\gamma}]_{\beta,\gamma=f,+, -}$ used in equations (44)–(52). Substituting the standard expressions for the electrochemical potentials into equation (59), we find:

$$\mathbf{i} = \left(-F \sum_{\gamma=f,+, -} z^\gamma \sum_{\beta=f,+, -} \mathbf{L}^{\beta\gamma} \cdot (\bar{V}^\beta \nabla_0 p + RT \nabla_0 \ln a^\beta) \right) - \mathbf{L}_e \cdot \nabla_0 \xi \quad (61)$$

with

$$\mathbf{L}_e = f^2 \sum_{\gamma=f,+, -} \sum_{\beta=f,+, -} z^\gamma z^\beta \mathbf{L}^{\beta\gamma} \quad (62)$$

the electrical conductance. At uniform temperature and pressure, when $\mathbf{i}=0$, the electrical potential gradient is given by:

$$-\nabla_0 \xi = RT \sum_{\beta=f,+, -} \mathbf{T}^\beta \cdot \nabla_0 \ln a^\beta \quad (63)$$

with $\mathbf{T}^\beta$ the reduced electrical transport tensor of component β :

$$\mathbf{T}^\beta = F \mathbf{L}_e^{-1} \cdot \sum_{\gamma=f,+, -} z^\gamma \mathbf{L}^{\beta\gamma} \quad (64)$$

in analogy to the reduced electrical transport number introduced by Staverman [10], an integrated form of equation (63) is

$$\xi_2 - \xi_1 = -RT \int_1^2 \sum_{\beta=f,+, -} [\mathbf{n}_0 ds_0 \cdot \mathbf{T}^\beta \cdot \nabla_0 \ln a^\beta] \quad (65)$$

in which $\mathbf{n}_0 ds_0$ is an infinitesimal segment of the path from 1 to 2, transformed back to the initial configuration. In the special case of a one-dimensional non-deforming medium equation (65) is the classic isothermal diffusion potential derived by Nernst [12, 13] and later by Staverman [10]. Note that the uncharged water is also included in the summation.

5. ELECTROKINETIC RELATIONSHIPS

The volume flux through the mixture is, in its Lagrangian form:

$$\mathbf{j} = \sum_{\gamma=f,+, -} n^\gamma \mathbf{v}^\gamma \quad (66)$$

or, if use is made of equation (45) equation (60), we find

$$\mathbf{j} = - \sum_{\gamma=f,+, -} \bar{V}^\gamma \sum_{\beta=f,+, -} \mathbf{L}^{\beta\gamma} \cdot \bar{V}^\beta \nabla_0 \mu^\beta. \quad (67)$$

Substituting the standard expressions for the electrochemical potentials into equation (67), we find:

$$\mathbf{j} = - \sum_{\gamma=f,+, -} \bar{V}^\gamma \sum_{\beta=f,+, -} \mathbf{L}^{\beta\gamma} \cdot (Fz^\beta \nabla_0 \xi + RT \nabla_0 \ln a^\beta) - \mathbf{L}_p \cdot \nabla_0 \quad (68)$$

with

$$\mathbf{L}_p = \sum_{\gamma=f,+, -} \sum_{\beta=f,+, -} \bar{V}^\gamma \bar{V}^\beta \mathbf{L}^{\beta\gamma} \quad (69)$$

If no gradients in chemical activities are assumed, equations (61) and (68) reduce to electrokinetic relationships:

$$\mathbf{j} = - \mathbf{L}^p \cdot \nabla_0 - \mathbf{L}^{pe} \cdot \nabla_0 \xi \quad (70)$$

$$\mathbf{i} = - \mathbf{L}^{pe} \cdot \nabla_0 - \mathbf{L}^e \cdot \nabla_0 \xi \quad (71)$$

in which

$$\mathbf{L}^{pe} = F \sum_{\gamma=f,+, -} \sum_{\beta=f,+, -} \bar{V}^\gamma z^\beta \mathbf{L}^{\beta\gamma}. \quad (72)$$

As a result of the symmetry of the equations (70) and (71), a three-dimensional form of the four Saxen's relations can be found. One connects streaming current to electro-osmotic pressure:

$$(\mathbf{j})_{\nabla_0 \xi = \mathbf{0}} \cdot (\nabla_0 p)_{\mathbf{j} = \mathbf{0}} = (\mathbf{i})_{\nabla_0 \xi = \mathbf{0}} \cdot (\nabla_0 \xi)_{\mathbf{j} = \mathbf{0}}; \quad (73)$$

one connects streaming potential and electro-osmotic flow:

$$(\mathbf{j})_{\nabla_0 p = \mathbf{0}} \cdot (\nabla_0 p)_{\mathbf{i} = \mathbf{0}} = (\mathbf{i})_{\nabla_0 p = \mathbf{0}} \cdot (\nabla_0 \xi)_{\mathbf{i} = \mathbf{0}}; \quad (74)$$

one connects second streaming potential and second electro-osmotic pressure:

$$(\mathbf{j})_{\mathbf{i} = \mathbf{0}} \cdot (\nabla_0 p)_{\mathbf{j} = \mathbf{0}} = (\mathbf{i})_{\mathbf{j} = \mathbf{0}} \cdot (\nabla_0 \xi)_{\mathbf{i} = \mathbf{0}}; \quad (75)$$

one connects second streaming current and second electro-osmotic flow:

$$(\mathbf{j})_{\nabla_0 p = \mathbf{0}} \cdot (\nabla_0 p)_{\nabla_0 \xi = \mathbf{0}} = (\mathbf{i})_{\nabla_0 \xi = \mathbf{0}} \cdot (\nabla_0 \xi)_{\nabla_0 p = \mathbf{0}}. \quad (76)$$

6. BIOT'S FINITE DEFORMATION THEORY OF POROUS MEDIA

Biot's theory [14] is obtained from the previous by skipping all the terms relating to the presence of fixed charges and ions. Conservation of mass follows from equation (19):

$$\nabla \cdot \mathbf{v}^s + \nabla \cdot (n^f(\mathbf{v}^f - \mathbf{v}^s)) = 0. \quad (77)$$

Conservation of momentum is obtained by substitution of equation (30) into equation (24):

$$\nabla \cdot \boldsymbol{\sigma}^{\text{eff}} - \nabla p = 0 \quad (78)$$

while the stress-strain relationship is given by equation (39):

$$\boldsymbol{\sigma}^{\text{eff}} = \frac{1}{J} \mathbf{F} \cdot \frac{\partial W}{\partial \mathbf{E}} \cdot \mathbf{F}^c \quad (79)$$

in which the strain energy function W depends only on local deformation. Darcy's law follows from equation (53):

$$n^f \mathbf{v}^{fs} = -\mathbf{K} \cdot \nabla_0 \left(p + \frac{\partial W}{\partial N^f} \right) \quad (80)$$

in which the term $\frac{\partial W}{\partial N^f}$ is interpreted for immiscible mixtures as the capillary pressure.

Equations (77)–(80) are Biot's equations of incompressible poroelasticity.

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