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Water films at grain-grain contacts: Debye-Hückel, osmotic model of stress, salinity, and mineralogy dependence

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Abstract—Water film diffusion is one of the mechanisms proposed to explain the deformation of rocks by pressure-solution during geological processes in the upper crust. This mechanism assumes that matter is dissolved inside the contact between two grains. The resulting solutes are transported in the pore fluid through diffusion in an adsorbed water film.

The main problem of this theory is that it requires the presence of a water film that is believed to be stable under large deviatoric stresses inside the contact between two grains. In this paper, we show that the electrically charged surface of a mineral can attract counter-ions from the pore and, by the related change of osmotic pressure, keep water within the contact. This is due to the counter ions in the water film that increase the salinity in the film relative to that in the pore. This lowers the free energy of water in the contact zone to a degree that balances the increase in free energy of water due to the elevated pressure in the film. These notions are made more precise by combining the theory of the Debye-Hückel double layer with equations of osmotic pressure. The resulting D-H/O theory predicts the dependence of the water film thickness on stress across the contact, composition of the pore fluid, and the identity of the minerals involved. Copyright © 1997 Elsevier Science Ltd

1. INTRODUCTION

Pressure solution is a major process of deformation of sedimentary rocks as well as endogeneous or metamorphic rocks in the first kilometers of the crust. It is thought that two different mechanisms are potentially able to explain the observed mass transfers. One suggests the dissolution of matter around the contact between two grains (Weyl, 1959; Barthust, 1958), the other assumes grain-boundary diffusion through a water film adsorbed inside the contact between two grains (Weyl, 1959; Rutter, 1976; Gratier and Guiguet, 1986).

A key problem in the theory of pressure solution is the nature of this water film that is believed to provide the reaction and transport medium in the water film diffusion (WFD) mechanism (Rutter, 1976; Spiers and Brzesowsky, 1993). To allow for WFD pressure solution, such a film must exist for large differences between the stress applied across the contact and the fluid pressure in the pore. Since the film is believed to be tens to hundreds of angströms thick (Horn et al., 1988; Low, 1992) and the evidence is that only one or two water layers can be tightly bound to a grain surface, it is perplexing to explain the existence of such films. Even if the film is icelike, the yield stress for ice is at most a few bars, far less than the hundreds of bars of deviatoric stress encountered in stressed contacts.

Many authors have demonstrated that a water film can be trapped between the sheets of some minerals such as clays and micas (Low, 1992; Sposito, 1992) or sapphires (Horn et al., 1988). Different forces act to keep water inside the minerals, particularly the double-layer force. We will use this theory to find a relationship between the electric surface charge on a mineral and the water film thickness.

2. THE PHYSICAL PICTURE

2.1. Structure of a Thin Film

In the theory of the pressure solution, the trapped fluid film can support a deviatoric pressure. There are two possibilities to explain this: first, this film is solid; second, the film is a liquid and some forces keep it inside the contact between two grains.

2.1.1. The solid film hypothesis

It might be asserted that the water film is icelike (or otherwise solid in structure) and can thereby sustain stress. Thus, for a solid model, the water film might be conjectured to exist when the stress normal to the contact is less than the fluid pressure inside the pore plus the yield stress. For ice, the latter is only a few bars and, hence, one expects that a solidlike water film failure model is not an adequate picture. Indeed, direct observations suggest that such a solidlike layer does not exceed a few angströms in thickness and is thereby one or two orders of magnitude less than generally accepted (or at least conjectured) layer thicknesses of ten to one hundred angströms.

2.1.2. The liquid film hypothesis

However, it might be asserted that the film is liquid. A charged mineral surface attracts a counterbalancing charge cloud in the solution as suggested in Fig. 1. Thus, the concentration of dissolved counterions near the surface exceeds that far from it. Osmotic equilibrium can then be set up with elevated fluid pressure developing in the region of appreciable counterbalancing charge density. The incoming water tends to displace the counterbalancing charge while the

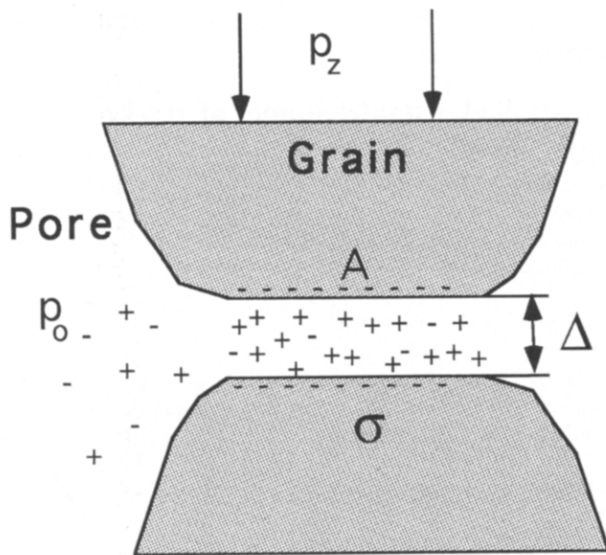


Fig. 1. Distribution of the electric charges in a schematic grain-grain contact. Here the negative charges of the surface of the grain are compensated by a cloud of positive ions in the water film of the contact. The compressive stress in the grain across the contact is p_z , the pressure of the pore fluid is p_o , σ is the electric charge per unit area, A , the surface of the contact, and Δ , the water film thickness.

strong Coulombic attraction keeps the counterbalancing charge localized near the surface. Thus a layer of compressed fluid is created near the grain surface. The osmotic layer is bound, yet still a liquid. In this way a true liquid water film (and not a solid one) can exist within a stressed grain contact.

2.2. Electric Surface Charge

Many minerals have surface charge which can be created by three different mechanisms:

- 1) Chemical reaction at the surface of the mineral can modify its electroneutrality. For example, in quartz, the (Si-OH) group can gain or lose a proton to become charged (Stumm and Morgan, 1981; Brady, 1992). In this case, the charge depends strongly on the pH. In the same way, clays in contact with water can gain negative charges by losing cations which go in solution. The mechanisms of these reactions are controlled by the rates of complexations and ionizations at the surface of the solid (van Cappellen et al., 1993).
- 2) Surface charge may be caused by lattice imperfections at the surface of the crystal and substitutions in the silicate framework. For example, if Al^{3+} replaces Si^{4+} in a tetrahedral site, a positive charge is lost, and the surface becomes negative. This mechanism appears in phyllosilicates (smectites, micas) and makes their surface charged.
- 3) A surface charge may also be established by adsorption of a surfactant ion, because of Van der Waals attractions or H bonds (Stumm and Morgan, 1981).

Different methods have been used to measure the surface charge of minerals. In many of them, the adsorption of com-

pensating ions is studied to estimate the concentration of charges on the mineral surface (Anderson and Sposito, 1991; van Cappellen et al., 1993). Few experiments have been done, and there is a lack of surface charge data for many minerals. Table 1 shows data for some common minerals.

3. SIMPLE MODEL

A simple model of the Debye-Hückel/Osmotic (D-H/O) layer for a stressed contact is suggested in Fig. 1. Electric charges are fixed at the surface of the mineral. In our example, these negative charges attract a swarm of positive charges from the pore fluid to reach electroneutrality inside the contact. This creates a difference of osmotic pressure between the contact fluid and the pore fluid, and the difference between p_z (the stress across the contact) and p_o (the pore fluid pressure) is set equal to the classical osmotic pressure:

$$p_z - p_o = -\frac{RT}{\bar{V}_w} \ln \left(\frac{x_w}{x_{w0}} \right) \quad (1)$$

where \bar{V}_w ($m^3 \cdot mole^{-1}$) is the molar volume of water, and x_w and x_{w0} are the mole fractions of water within the contact and within the pore fluid, respectively. By definition, the mole fraction x_w is equal to $(n_w/n_w + n_s)$ where n_w and n_s are the number of moles of water and all the solutes, respectively.

In this first model, the simplifying assumption is made that the counterbalancing charge is spread out uniformly within the contact. If σ is the surface charge per unit area

Table 1. Surface charge for different minerals. These data are strongly pH-dependent.

Mineral	Surface charge (Coulomb $\cdot m^{-2}$)	pH range	Ref.
Alumina	0; -0.06	4; 11	(1)
Alumina	0.3; 0	3; 6.5	(3)
Alumina	0; -0.3	6.5; 10	(3)
Amorphous silica	-0.0048	5	(2)
Amorphous silica	-0.048	7	(2)
Amorphous silica	-0.48	11	(2)
Silica	0; -0.75	4; 10	(4)
Silica	-0.48; -0.96	>2.5	(5)
Montmorillonite	0.12; 0	0; 2	(6)
Montmorillonite	0; -0.2	2; 4	(6)
Montmorillonite	0.12	—	(8)
Smectites	-0.12; -0.17	—	(8)
Kaolinite (edge)	0; -1.2	3.5; 10	(1)
Kaolinite (edge)	-0.6	7	(1)
Kaolin	-0.18; +0.63	0-10	(9)
Muscovite	-0.81; +0.54	3; 9	(9)
MnCO ₃	1.45; 0	4; 5.5	(7)
MnCO ₃	0; -1.98	5.5; 8	(7)
CaCO ₃	1.45; 0	6; 8	(7)
CaCO ₃	0; -1.45	8; 12	(7)
CaCO ₃	0.1; 0	6; 8	(6)
CaCO ₃	0; -0.2	8; 10	(6)

References: (1) Zhou and Gunter (1992), (2) Brady (1992), (3) Brady (1994), (4) Yates and Healy, (1975), (5) Baudin et al. (1990), (6) Stumm and Morgan (1981), (7) van Cappellen et al. (1993), (8) Villemure (1990), (9) Herrington et al. (1992).

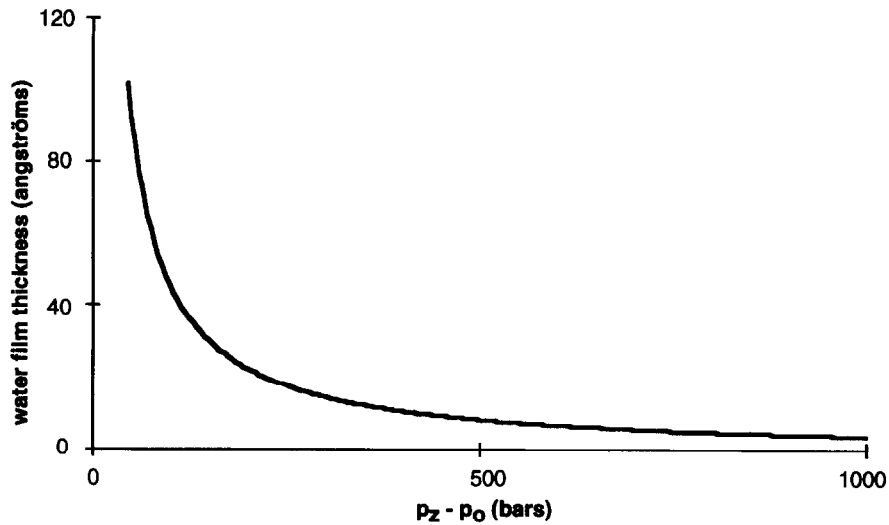


Fig. 2. Preliminary prediction of water film thickness Δ as a function of the difference between the compressive stress p_z normal to the contact and fluid pressure p_o in the pore, for a temperature of 100°C. A negative charge density of -0.1 C.m^{-2} , characteristic of quartz at a pH between 8 and 10, was chosen (see Table 1).

and Δ is the water film thickness, then the concentration of (uniformly smeared) compensating charge within the contact is $2\sigma/F\Delta$, the 2 coming from the assumption that the grain surface on either side of the contact has the same charge. F represents Faraday's constant. Then if C_o is the total molar concentration (mole.m⁻³) of all charged solutes within the pore, one has

$$x_w = \frac{1}{1 + \bar{V}_w \left(C_o + \frac{2\sigma}{F\Delta} \right)}, \quad x_{w_o} = \frac{1}{1 + \bar{V}_w C_o} \quad (2)$$

Combining Eqn. 1 and 2, we may determine Δ as a function of $p_z - p_o$:

$$\Delta((p_z - p_o), C_o, \sigma, T) = \frac{2\sigma}{F(\bar{V}_w C_o + 1) \left\{ \exp \left(\frac{\bar{V}_w (p_z - p_o)}{RT} \right) - 1 \right\}} \quad (3)$$

Thus one determines the predicted water film thickness as a function of contact normal stress, salinity, and temperature.

Results for Δ as a function of the differential pressure are seen in Fig. 2. In this example, the electrolyte is a solution of Na⁺ and Cl⁻. The concentration in the pore fluid is like seawater. We have neglected the concentrations of ions such as H⁺ and OH⁻ because they are low compared to Na⁺ and Cl⁻. The surface charge is set equal to -0.1 C.m^{-2} , observed for quartz in the pH range 8–10 (Yates and Healy, 1975).

The water film thicknesses are close to those expected (Horn et al., 1988; Pashley and Israelachvili, 1984). Furthermore, the water film is appreciable (several Å), even when $(p_z - p_o)$ is hundreds of bars. This latter stability is needed if pressure solution is expected to operate at several km depth in a sedimentary basin. For example, at a 5 km depth, p_z is 1250 bars, and p_o value may range from an hydrostatic value (500 bars) to the lithostatic value. So, $(p_z - p_o)$ may

range between 0 and more than 750 bars if the stress concentrates on grain contacts. Experiments on quartz (Gratier and Guiguet, 1986; Gratier, 1993) clearly show that pressure solution may develop under large $(p_z - p_o)$ values (3000–4000 bars). Thus, the exsolution of this thin film must be tested over a large range of $(p_z - p_o)$. We believe the theory will be able to predict the variations of Δ with mineral identity, presence/absence of clay in the contact, pore fluid salinity, pH, and temperature.

4. DEBYE-HÜCKEL/OSMOTIC MODEL

While the simple model results are encouraging, several questions emerge.

- 1) The distribution of compensating charge is not uniform. Could it be distributed according to the Debye-Hückle double layer theory?
- 2) Will the elevated pressure in the osmotic layer have a complex effect on the D-H layer structure—attracting ions with negative partial molar volumes and expelling solutes with positive ones?
- 3) What happens when the surface charge is pH or otherwise fluid composition dependent?

In the present model, we address only the first two issues.

The voltage V within the water film satisfies Poisson's equation

$$\frac{d^2V}{dz^2} = - \frac{4\pi F}{\epsilon_w} \sum_{\alpha=1}^N z_\alpha c_\alpha \quad (4)$$

where z is distance across the film (lying within $-\Delta/2 < z < +\Delta/2$). The dielectric constant of water ϵ_w is taken to be constant ($6.71 \times 10^{-10} \text{ C/V/m}$); F is Faraday's constant (96484.6 C/mol) and c_α is the concentration of solute α in the aqueous solution and z_α is its valence.

An overall equilibrium is assumed between the pore fluid and the contact fluid. If μ_α is the chemical potential of species α ($\alpha = 1, 2, \dots, N, w$; w being H_2O , the solvent) inside the contact and $\mu_{\alpha o}$, the chemical potential in the pore fluid, then the aforementioned equilibrium implies

$$\mu_\alpha(p, T, c) = \mu_{\alpha o}(p_o, T, c_o) \quad (5)$$

where $c = \{c_1, c_2, \dots, c_N, c_w\}$ and $c(z)$ and $p(z)$ are to be determined from the D-H osmotic theory. Here, p represents the pressure inside the contact and can vary with z .

In order to simplify the calculations, first assume the solution is dilute (the effect of Pitzer-type corrections were also used—see Appendix). For the solutes, therefore, one has

$$\mu_\alpha = \mu_\alpha^* + p\bar{V}_\alpha + RT \ln a_\alpha + z_\alpha FV - RTu_o \exp\left(\frac{z - \lambda_1}{\lambda_2}\right); \quad \alpha \neq w \quad (6)$$

where $a_\alpha = \gamma_\alpha c_\alpha$, for reference potential, μ_α^* . a_α is the activity of the species α , γ_α , the activity coefficient. The last term is a molecular potential contribution (see below). Taking $V = 0$ in the pore, the equilibrium (5) yields

$$a_\alpha = a_{\alpha o} \exp\left\{-\frac{[(p - p_o)\bar{V}_\alpha + z_\alpha FV]}{RT}\right\} \quad (7)$$

Thus the c_α in Eqn. 4 can be eliminated. A further equation needed to yield $p(z)$ is obtained from the osmotic condition. For water we assume

$$\mu_w = \mu_w^* + p\bar{V}_w + RT \ln a_w + RTu_o \exp\left(\frac{z - \lambda_1}{\lambda_2}\right) \quad (8)$$

Equilibrium between the pore and the film then yields the $u_o \exp[(z - \lambda_1)/\lambda_2]$ term represents a repulsion potential, z being the distance from the surface of the mineral. It is known that on every mineral surface, one layer of water is strongly attached, and it is difficult to remove it. The potential, with $\lambda_1 = 2 \text{ \AA}$ and $\lambda_2 = 0.1 \text{ \AA}$, allows a strong binding of a monolayer of water molecules on the mineral surface. Thus, a minimum thickness of about 4 \AA for the water film is preserved. Therefore, this potential takes into account the fact that adsorption calculations show that the last layer on a quartz crystal can withstand pressures up to 7000 bars (Every et al., 1961; de Boer, 1977). The value of u_o is chosen so that for $z = 0$, the repulsive potential is equal to RT_d , where T_d represents the temperature of dewatering for the quartz (in the range of 600–700 K).

From Eqns. 4 to 8, we have

$$(p - p_o) = RT \ln\left(\frac{a_w}{a_o}\right) - RTu_o \exp\left(-\frac{z - \lambda_1}{\lambda_2}\right) \quad (9)$$

The activity of water, a_w , is calculated through the osmotic coefficient once all the concentrations c_α are known. c can be expressed in terms of a_w by combining Eqns. 7 and 9 to obtain

$$\gamma_\alpha c_\alpha = \gamma_{\alpha o} c_{\alpha o} \left(\frac{a_w}{a_{w o}}\right)^{\bar{V}_\alpha/\bar{V}_w} \exp\left(-\frac{z_\alpha FV}{RT}\right) \exp\left[\left(\frac{\bar{V}_\alpha}{\bar{V}_\alpha + \bar{V}_w} + 1\right) u_o \exp\left(-\frac{z - \lambda_1}{\lambda_2}\right)\right] \quad (10)$$

Therefore Eqn. 10 is a nonlinear algebraic equation for a_w in terms of $c_{\alpha o}$, all the c_α and V once the dependence of a_w and γ_α on c is delineated. This equation is written for all the species α . We solve the resulting system of nonlinear equations by iteration.

In this way, the D-H osmotic problem is reduced to solving Poisson's equation for V with a c_α -dependent charge density coupled to a system of nonlinear algebraic equations relating the c_α and V . This nonlinear problem can be solved numerically in one dimension via an iteration scheme.

To complete the calculation, we need to consider various types of boundary conditions. Conditions on the voltage at $z = \pm\Delta/2$ needed to solve Poisson's equation may be obtained by integrating Poisson's equation across the fixed charge sheet, assumed to reside at $z = \pm\Delta/2$. Thus, Poisson's equation is augmented to be

$$-\frac{\epsilon_w}{4\pi} \frac{d^2V}{dz^2} = \sum_{\alpha=1}^N z_\alpha c_\alpha + \frac{\sigma}{F} \left[\delta\left(z - \frac{\Delta}{2}\right) + \delta\left(z + \frac{\Delta}{2}\right) \right] \quad (11)$$

Integrating over a small interval about $z = +\Delta/2$ yields

$$-\frac{\epsilon_w}{4\pi} \left\{ \frac{dV}{dz} \left(\frac{\Delta}{2} + 0^+\right) - \frac{dV}{dz} \left(\frac{\Delta}{2} + 0^-\right) \right\} = \frac{\sigma}{F} \quad (12)$$

where 0^+ and 0^- are positive and negative infinitesimals, respectively. But inside the grain ($z > \Delta/2$), there are no charges so that V is constant and, hence, dV/dz is zero there. Thus, we have

$$\frac{dV}{dz} \left(\frac{\Delta}{2} + 0^-\right) = \frac{4\pi\sigma}{\epsilon_w F} \quad (13)$$

Another boundary condition is a condition of symmetry about $z = 0$, where $dV/dz = 0$. With this condition, we assume that the two mineral surfaces are identical, so the concentration and voltage profiles are symmetric across the water film.

It might be questioned as to whether the compensating charge actually balances the surface charge. Integrating Poisson's equation over the interval $-\Delta/2 + 0^+ < z < +\Delta/2 + 0^-$, i.e., over the whole film Δ but not including the fixed charge layer, and using the boundary conditions on dV/dz at $\pm\Delta/2 + 0^+$, one obtains

$$\int_{-\Delta/2+0^+}^{\Delta/2+0^-} dz \sum_{\alpha=1}^N z_\alpha c_\alpha = \frac{2\sigma}{F} \quad (14)$$

Thus the charge within the water film is exactly compensated.

4.1. Thermodynamics of the Relation Between Δ and P_z

The calculation of the dependence of Δ on p_z must be done through a careful consideration of the thermodynamics of the water film. In particular, we now show that the compressive stress applied to the solid across the water film, p_z , must be obtained as the derivative of an appropriate free energy with respect to Δ .

The compression of the water film is carried out at con-

stant chemical potential and temperature. Thus, we seek a free energy whose derivative with respect to volume (and ultimately Δ) is the pressure doing the overall ("piston") compression—i.e., p_z . The Gibb's free energy of the film considered as a totality, G^{film} , is related to the piston pressure p_z , the total number of moles n_α^{film} , and temperature via Euler's theorem

$$G^{\text{film}}(p_z, \{n_\alpha^{\text{film}}\}, T) = \sum_{\alpha=1}^N n_\alpha^{\text{film}} \mu_\alpha^{\text{film}} \quad (15)$$

and, furthermore,

$$dG^{\text{film}} = \sum_{\alpha=1}^N n_\alpha^{\text{film}} d\mu_\alpha^{\text{film}} + V^{\text{film}} dp_z - S^{\text{film}} dT \quad (16)$$

On the other hand, the transformed function Ω^{film} ,

$$\Omega^{\text{film}} = G^{\text{film}} - \sum_{\alpha=1}^N n_\alpha^{\text{film}} \mu_\alpha^{\text{film}} - p_z V^{\text{film}} \quad (17)$$

has increment

$$d\Omega^{\text{film}} = \sum_{\alpha=1}^N n_\alpha^{\text{film}} d\mu_\alpha^{\text{film}} - p_z dV^{\text{film}} - S^{\text{film}} dT \quad (18)$$

Thereby,

$$p_z = - \left(\frac{\partial \Omega^{\text{film}}}{\partial V^{\text{film}}} \right)_{\mu^{\text{film}}, T} \quad \text{where } \mu^{\text{film}} = (\mu_1, \mu_2, \dots, \mu_N) \quad (19)$$

For the film of area A , $V^{\text{film}} = A\Delta$ and, hence,

$$p_z = - \frac{1}{A} \left(\frac{\partial \Omega^{\text{film}}}{\partial \Delta} \right)_{\mu, T} \quad (20)$$

a key result of the D-H/Osmotic theory.

The macroscopic thermodynamics of Eqns. 4–9 can now be related to the mesoscopic theory of the previous section as follows. In every volume element, we define the free energies G and Ω as above:

$$G = \sum_{\alpha=1}^N n_\alpha^{\text{film}} \mu_\alpha^{\text{film}} \quad (21)$$

$$\Omega = G - \sum_{\alpha=1, \alpha \neq W}^N n_\alpha \mu_\alpha - pV = -pV \quad (22)$$

Then the Ω -energy density $\omega = \Omega/V$ can be used to obtain Ω by integrating over the film

$$\Omega^{\text{film}} = \int_{\text{film}} \omega d^3r = - \int_{\text{film}} p d^3r \quad (23)$$

Then, using $d^3r = Adz$, we obtain via Eqn. 20

$$p_z = \frac{\partial}{\partial \Delta} \left(\int_{-\Delta/2}^{+\Delta/2} p(z, \Delta) dz \right)_{\mu, T} \quad (24)$$

Note that as $p(z, \Delta)$ depends on Δ through the solution of the D-H/Osmotic model, p_z is not simply $[p(\Delta/2, \Delta)$

$+ p(-\Delta/2, \Delta)]/2$. Rather, p_z depends on the distribution of p across the entire film (i.e., $-\Delta/2 < z < +\Delta/2$).

5. RESULTS AND DISCUSSION

5.1. Poisson's Equation

Profiles of voltage and concentration across the water film are shown in Fig. 3. In this example, the grains are made of quartz, and the fluids contain only Na^+ and Cl^- . These profiles are symmetric because quartz bounds both sides of the water film.

As the surface charge is negative in our example, the concentration of the compensating ion, Na^+ , is high near the mineral surface. The concentration of Cl^- is low in the same region. In the middle of the water film, the two concentrations are equal because of electroneutrality. The voltage decreases from a value of -0.11 V near the grain to -0.0001 V in the middle of the water film.

5.2. The Relationship Between the Pressure and the Water Film Thickness

If we calculate the pressures corresponding to different Δ 's in Eqn. 24, we obtain a curve like that in Fig. 4. In double logarithmic scales, the curves can be fitted by straight lines. We obtain a linear relationship between the logarithms of the differential pressure (bars) and Δ (ångströms):

$$\ln(\Delta) = a + b \ln(p_z - p_o) \quad (25)$$

where a and b are constants depending on surface charge, temperature, and pore fluid salinity. We have calculated such curves for different surface charges between -0.01 and -0.15 C.m^{-2} , which are typical values for common minerals (see Table 1), at constant temperature (25°C) and found the charge dependence of a and b to be

$$a = 9.3925 + 5.88 \sigma + 26.96 \sigma^2$$

$$b = -1.008 - 0.41 \sigma$$

where σ is the surface charge (C.m^{-2}).

To compare these results with the simple model of Eqn. 3, we develop the exponential in Eqn. 3 and obtain

$$\Delta = \frac{C}{p_z - p_o} \quad (26)$$

where C is a constant. In the complete Debye-Hückel/Osmotic model, we have

$$\Delta = C'(p_z - p_o)^b \quad (27)$$

where C' is a constant and b has a value close to -1 . The two equations, (26) and (27), are similar. The only difference is the value of the constants C and C' . $C = 5 \times 10^{-8}$ and $C' = 8 \times 10^{-7}$ for $(p_z - p_o)$ in bars and Δ in m. There is a factor 16 between these two numbers. At the same pressure, the full DH/O theory gives a bigger water film thickness.

5.3. The Limits of the Model

The purpose of this study was to estimate the influence of electric charge spread on the surface of the grain on the

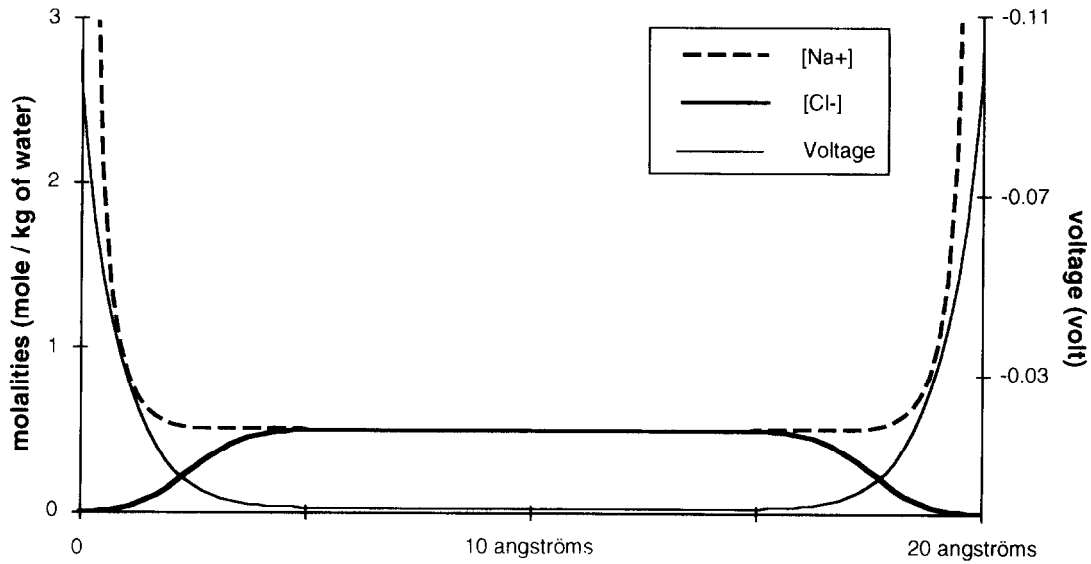


Fig. 3. Profile of the voltage and the concentrations inside the contact, across the water film. Parameters used to solve Eqns. 4 and 10 were $\sigma = -0.05 \text{ C.m}^{-2}$, concentration in the pore fluid 0.5 mol/kg of water, $T = 298 \text{ K}$, and $\Delta = 20 \text{ \AA}$.

water film inside the contact between two grains. We have obtained a relationship between the thickness of the film of water, pressure, temperature, and the surface charge for a simple case where the two minerals along the contact are the same. This relationship should change if the two surface charges are different, for example, if a grain of quartz is in contact with a sheet of mica. In such a case, the symmetry in the profiles of concentration and voltage of Fig. 3 can be skewed toward one of the minerals.

Many points have not yet been studied. Particularly, the influence of temperature on the thickness of the water film (through the dielectric constant and the activity coefficients) may not be negligible. Another problem is the roughness of the mineral surface. We assumed that the surface of contact was flat. This may be a fair estimation for micas sheets, but

it becomes less realistic in the case of quartz. The problem of the variations of the surface charge can be raised, too. Many authors underline that the surface charge on a mineral is pH-dependent and also temperature dependent (Yates and Healy, 1975; Sposito, 1992), but the variation of the surface charge with depth is not well-known.

From Eqn. 3, it is seen that the salinity of the formation does not have a big effect unless the concentrations are very high, near the saturation with respect to NaCl. The consequence of this statement is that pressure solution should be less efficient when the pore fluid is high-concentrated.

6. CONCLUSIONS

The aim of this paper was to evaluate the influence of pressure on the water film thickness inside the contact between two grains. The electric charges on the mineral surface inside the contact attract counterbalancing ions from the pore fluid. This creates a difference of osmotic pressure between the fluid inside the contact and the pore fluid which can preserve a film of water. The result of our model based on the Debye-Hückel theory is a linear relationship between the logarithms of the thickness of the water film on one hand and the difference between the stress applied on the grain and the fluid pressure in the pore on the other hand.

This study has shown that a high level of stress can be induced on mineral surfaces due to the osmotic effect. This phenomenon preserves a film of water inside the contact under high effective pressures and activates the water film diffusion mechanism. This may be a first attempt to explain why pressure solution seems to be more important in sedimentary rocks containing clays. These minerals can have a large surface charge which increases the water film thickness and so activates the WFD pressure solution.

On the opposite, this theory predicts that for a nil electric surface charge, the water film thickness is close to zero. The

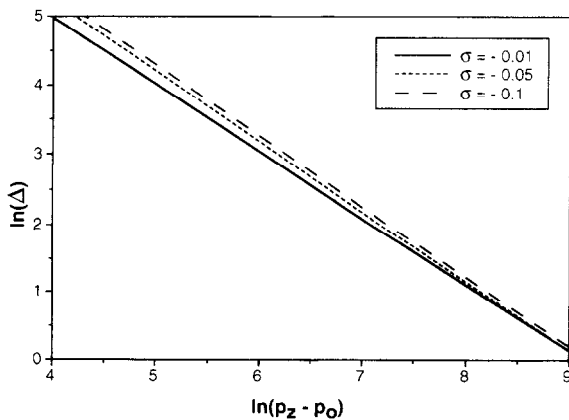


Fig. 4. Dependence of water film thickness on deviatoric stress ($p_z - p_o$) for a range of surface charge densities according to the D-H/O model. The curves are in double logarithm scales. Δ is in \AA , ($p_z - p_o$) is in bars.

surface charge of a mineral is highly dependent on the pH of the water and is nil near the point of zero net charge. In this case, the water film thickness should be zero and the pressure solution less efficient. This could be an element of explanation as to why some rocks deform by pressure-solution whereas other in very close conditions do not.

Another point is the decrease of the water film thickness with increasing pressure. Our model could explain the diminution of pressure solution in sedimentary basins for depths greater than 3000 or 4000 meters, where the effective stress is so high that the water film is only several angstroms thick and the WFD slows down. This is false when the fluid pressure increases to reach a lithostatic value. In this case, a thick fluid film is preserved and pressure solution can be efficient at 10–15 km, even in rocks like granites (Burg and Ponce, 1985)

Thus, it is concluded that a water film can be trapped inside the contact between two grains and that can be an argument for the WFD mechanism during pressure-solution.

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APPENDIX: THE THERMODYNAMIC PROPERTIES OF THE SOLUTION USING PITZER EQUATIONS

In all the calculations of this paper, we assume that the compensating ions in the solution are Na⁺ and Cl⁻. In fact, we use relatively high concentrations in the pore fluid (as in seawater). The effects of ions such as H⁺ or OH⁻ are neglected because of their low concentrations. To calculate the activities, we use a Pitzer approach. Pitzer and co-workers have developed a set of equations that describe the thermodynamic properties of electrolyte solutions (Pitzer and Mayorga, 1973; Pitzer, 1973, 1987, 1991). These equations are based on an extended Debye-Hückel theory.

Table A1. Values of Pitzer's model parameters.

$\beta_{\text{NaCl}}^{(0)}$ (kg/mole)	$\beta_{\text{NaCl}}^{(1)}$ (kg/mole)	$C_{\text{NaCl}}^{\phi} = 2C_{\text{NaCl}}$ (kg ² /mole ²)
0.0764	0.277	0.0014

The case of a solution of NaCl has been studied in detail (Pitzer et al., 1984). The osmotic coefficient for water (ϕ), and the logarithms of the activities of sodium (γ_{Na}) and chloride (γ_{Cl}) ions are given in the following equations:

$$\phi - 1 = \frac{2}{m_{\text{Na}} + m_{\text{Cl}}} \left[\frac{-A^{\phi} I^{3/2}}{1 + bI^{1/2}} + m_{\text{Na}} m_{\text{Cl}} (B_{\text{NaCl}}^{\phi} + Z C_{\text{NaCl}}) \right] \quad (\text{A1})$$

where b is a universal parameter with the value $1.2 \text{ kg}^{1/2} \cdot \text{mole}^{-1/2}$, and are the molalities (mole/kg of solvent) of Na^+ and Cl^- , respectively and I is the ionic strength of the solution. By definition in this case

$$I = \frac{1}{2} (m_{\text{Na}} + m_{\text{Cl}}) \quad (\text{A2})$$

The activity of water $a_{\text{H}_2\text{O}}$ is easily expressed by the osmotic coefficient (Wood, 1975).

$$\ln (a_{\text{H}_2\text{O}}) = - \frac{m_{\text{Na}} + m_{\text{Cl}}}{55.51} \phi \quad (\text{A3})$$

$$\ln (\gamma_{\text{Na}}) = F + m_{\text{Cl}} (2B_{\text{NaCl}} + Z C_{\text{NaCl}}) + m_{\text{Na}} m_{\text{Cl}} C_{\text{NaCl}}$$

$$\ln (\gamma_{\text{Cl}}) = F + m_{\text{Na}} (2B_{\text{NaCl}} + Z C_{\text{NaCl}}) + m_{\text{Na}} m_{\text{Cl}} C_{\text{NaCl}} \quad (\text{A4})$$

F is a Debye-Hückel term depending only on the ionic strength, which describes long range interactions between the ions. The other terms, B_{NaCl} and C_{NaCl} , take in account short range interactions between Na^+ and Cl^- . The functions F and Z are defined by:

$$F = f^{\gamma} + m_{\text{Na}} m_{\text{Cl}} B_{\text{NaCl}}^{\phi} \quad (\text{A5})$$

where

$$f^{\gamma} = -A^{\phi} \left(\frac{I^{1/2}}{1 + bI^{1/2}} + \frac{2}{b} \ln (1 + bI^{1/2}) \right) \quad (\text{A6})$$

$$Z = m_{\text{Na}} + m_{\text{Cl}} \quad (\text{A7})$$

A^{ϕ} is the Debye-Hückel parameter ($0.3915 \text{ kg}^{1/2} \cdot \text{m}^{-1/2}$ at 25°C)

$$A^{\phi} = \frac{1}{3} \left(\frac{2\pi N_A \rho_w}{1000} \right)^{1/2} \left(\frac{e^2}{k\epsilon_w T} \right)^{3/2} \quad (\text{A8})$$

with N_A , Avogadro's number; e , the electronic charge, k , Boltzmann's constant, ρ_w and ϵ_w , the density and dielectric constant of pure water. These last two parameters are sensitive to pressure and temperature. Bradley and Pitzer (1979) have fitted the variations of the dielectric constant of water with P and T .

The parameter A^{ϕ} has been studied by many authors (Ananthaswamy and Atkinson, 1984; Archer, 1990; Bradley and Pitzer, 1979) but for practical calculations, one can use the equation for A^{ϕ} given by Clegg and Whithfield (1991) for a temperature between 273 and 373K.

$$A^{\phi} = 0.13422 (4.1725332 - 0.1481291 T^{0.5} + 1.518805 \times 10^{-5} T^2 - 1.8016317 \times 10^{-8} T^3 + 9.3816144 \times 10^{-10} T^{3.5}) \quad (\text{A9})$$

Terms B_{NaCl} in the former equations depend on the ionic strength. Pitzer (1991) gives the expressions of these parameters.

$$B_{\text{NaCl}}^{\phi} = \beta_{\text{NaCl}}^{(0)} + \beta_{\text{NaCl}}^{(1)} \exp(-\alpha I^{1/2}) \quad (\text{A10})$$

$$B_{\text{NaCl}} = \beta_{\text{NaCl}}^{(0)} + \beta_{\text{NaCl}}^{(1)} g(-\alpha I^{1/2}) \quad (\text{A11})$$

$$B_{\text{NaCl}}^{\prime} = \frac{\beta_{\text{NaCl}}^{(1)} g'(-\alpha I^{1/2})}{I} \quad (\text{A12})$$

$\alpha = 2$ and the functions $g(x)$ and $g'(x)$ are

$$g(x) = \frac{2}{x^2} (1 - (1+x)e^{-x}) \quad (\text{A13})$$

$$g'(x) = \frac{2}{x^2} \left(1 - \left(1 + x + \frac{x^2}{2} \right) e^{-x} \right) \quad (\text{A14})$$

The values of $\beta_{\text{NaCl}}^{(0)}$, $\beta_{\text{NaCl}}^{(1)}$, C_{NaCl}^{ϕ} , and C_{NaCl} at 25°C and 1 bar, have been measured. Pitzer (1984) gives the variations of these parameters with the temperature (between 273 and 573K), the pressure (between 1 bar and 1 kbar), for ionic strength less than 6 mole/kg (Table A1).