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CHEMISTRY OF WATER EXPELLED FROM COMPACTING CLAY LAYERS: A MODEL BASED ON DONNAN EQUILIBRIUM

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ABSTRACT

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Equations are derived to follow the chemistry of solutions expelled from compacting clay suspensions which contain a uni-univalent electrolyte. The separated equilibrium solution contains more electrolytes due to negative adsorption of the charged clay minerals with compaction. Comparison with experimental data indicates that relatively low activity coefficients in the suspension tend to counterbalance this effect.

INTRODUCTION

The electrolyte content of water expelled by pressure from clay suspensions generally is higher than is calculated from the amount of salt added to the original amount of water in the colloidal system (Bolt, 1961b; Kryukov, 1967). Likewise, the electrolyte content of a colloidal suspension is known to decrease during compaction (von Engelhardt and Gaida, 1963; Rieke and Chilingarian, 1974). This "negative adsorption" is caused by the preferential expulsion of ions of the same sign of charge as the colloids, when compaction brings the latter closer to each other.

Equations describing the negative adsorption as a function of the remaining water content of a suspension have been derived from a direct application of the Donnan equilibrium and from a more precise location of the phenomenon at the surface of colloidal particles by means of Gouij-Chapman theory by Bolt (1961a). However, to explain his experimental data, Bolt had to assume that hyperfiltration occurred over the filters that were used. In the present communication an explanation is sought in non-ideal behaviour, expressed in activity coefficients.

THE DONNAN EQUILIBRIUM

The potential differences between a clay paste and its supernatant liquid, which are substantiated by the so-called suspension effect (Overbeek, 1956), allow to apply the classical Donnan equation to such a system. Fig. 1 illustrates the system, with the suspension having a potential ψ^{I}, a (negative) charge due to colloidal particles of x (equiv./l), and a salt concentration $m_{\mathrm{Cl}}^{\mathrm{I}}$ (equiv./l), and with the supernatant liquid having a potential ψ^{II} and salt concentration $m_{\mathrm{Cl}}^{\mathrm{II}}$.

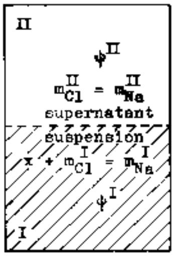

Fig.1. Basic components of the Donnan suspension.

Now, the electrochemical potentials μ of Cl$^-$ are respectively (Donnan and Guggenheim, 1932):

$$\mu_{\mathrm{Cl}}^{\mathrm{I}} = \mu_{\mathrm{Cl}}^{0} + RT \ln \gamma_{\mathrm{Cl}}^{\mathrm{I}} m_{\mathrm{Cl}}^{\mathrm{I}} - F\psi^{\mathrm{I}} \tag{1}$$

$$\mu_{\mathrm{Cl}}^{\mathrm{II}} = \mu_{\mathrm{Cl}}^{0} + RT \ln \gamma_{\mathrm{Cl}}^{\mathrm{II}} m_{\mathrm{Cl}}^{\mathrm{II}} - F\psi^{\mathrm{II}} \tag{2}$$

with F = Faraday constant and μ_i^0 = standard potential of i.

Also for the counter-ions in the system:

$$\mu_{\mathrm{Na}}^{\mathrm{I}} = \mu_{\mathrm{Na}}^{0} + RT \ln \gamma_{\mathrm{Na}}^{\mathrm{I}} m_{\mathrm{Na}}^{\mathrm{I}} + F\psi^{\mathrm{I}} \tag{3}$$

$$\mu_{\mathrm{Na}}^{\mathrm{II}} = \mu_{\mathrm{Na}}^{0} + RT \ln \gamma_{\mathrm{Na}}^{\mathrm{II}} m_{\mathrm{Na}}^{\mathrm{II}} + F\psi^{\mathrm{II}} \tag{4}$$

If the system is in equilibrium, $\mu_{\mathrm{Cl}}^{\mathrm{I}} = \mu_{\mathrm{Cl}}^{\mathrm{II}}$ and $\mu_{\mathrm{Na}}^{\mathrm{I}} = \mu_{\mathrm{Na}}^{\mathrm{II}}$, allowing eqs. 1—4 to be reduced to:

$$(\gamma_{\mathrm{Na}} m_{\mathrm{Na}} \gamma_{\mathrm{Cl}} m_{\mathrm{Cl}})^{\mathrm{I}} = (\gamma_{\mathrm{Na}} m_{\mathrm{Na}} \gamma_{\mathrm{Cl}} m_{\mathrm{Cl}})^{\mathrm{II}} \tag{5}$$

Electroneutrality requires:

$$\text{in phase I:} \qquad m_{\mathrm{Cl}}^{\mathrm{I}} + x = m_{\mathrm{Na}}^{\mathrm{I}} \tag{6}$$

$$\text{in phase II:} \qquad m_{\mathrm{Cl}}^{\mathrm{II}} \qquad = m_{\mathrm{Na}}^{\mathrm{II}} \tag{7}$$

Substituting eqs. 6 and 7 into eq. 5 gives the classical Donnan equation:

$$\frac{(\gamma_{\mathrm{Na}}\gamma_{\mathrm{Cl}})^{\mathrm{I}}}{(\gamma_{\mathrm{Na}}\gamma_{\mathrm{Cl}})^{\mathrm{II}}} (x + m_{\mathrm{Cl}}^{\mathrm{I}}) m_{\mathrm{Cl}}^{\mathrm{I}} = (m_{\mathrm{Cl}}^{\mathrm{II}})^2 \tag{8}$$

COMPACTION OF A DONNAN SUSPENSION

With an initial suspension volume V_0 with salt content s_0 (equiv.) and x_0 equiv./l charged colloids, the initial salt concentration is $m_{\mathrm{Cl}}^{\mathrm{I}} = s_0/V_0$. Compaction of the suspension from V_0 to V, with a corresponding change to $m_{\mathrm{Cl}}^{\mathrm{I}} = s/V$, and $x = V_0x_0/V$, gives for eq. 8, after taking the square root:

$$m_{\mathrm{Cl}}^{\mathrm{II}} = \frac{f}{V}\,[s(s + V_0x_0)]^{1/2} \tag{9}$$

where:

$$f^2 = \frac{(\gamma_{\mathrm{Na}}\gamma_{\mathrm{Cl}})^{\mathrm{I}}}{(\gamma_{\mathrm{Na}}\gamma_{\mathrm{Cl}})^{\mathrm{II}}} = \frac{\gamma_{\pm\,\mathrm{NaCl}}^{\mathrm{I}}}{\gamma_{\pm\,\mathrm{NaCl}}^{\mathrm{II}}}$$

Eq. 9 may be solved for two cases:

(1) During dropwise removal of the filtrate from the system with infinitesimal equilibration: $m_{\mathrm{Cl}}^{\mathrm{II}} = \mathrm{d}s/\mathrm{d}V$. This case is applicable to experimental setups where the filtrate is dropwise collected and removed from the system.

(2) With the mass balance: $m_{\mathrm{Cl}}^{\mathrm{II}} = (s_0 - s)/(V_0 - V)$, which seems more appropriate when the equilibrium solution is separated by centrifuging. In nature this corresponds with the burial of a clay-rich layer sandwiched between sandy layers, if mass flow other than due to compaction is negligible.

ad (1): Infinitesimal equilibration: $m_{\mathrm{Cl}}^{\mathrm{II}} = \mathrm{d}s/\mathrm{d}V$

Eq. 9 can be integrated from the initial volume of the suspension V_0 with salt content s_0 to V with salt content s:

$$\int_{s_0}^{s} \frac{\mathrm{d}s}{[s(s + V_0x_0)]^{1/2}} = f\int_{V_0}^{V} \frac{\mathrm{d}V/\mathrm{d}s}{V}\,\mathrm{d}s \tag{10}$$

with:

$$\frac{\mathrm{d}s}{[s(s + V_0x_0)]^{1/2}} = \frac{\dfrac{2}{V_0x_0}\,\mathrm{d}s}{\left[\left(\dfrac{2}{V_0x_0}\,s + 1\right)^2 - 1\right]^{1/2}}$$

the solution of eq. 10 is:

$$\operatorname{arccosh}\left(\frac{2\,s}{V_0x_0} + 1\right) - \operatorname{arccosh}\left(\frac{2\,s_0}{V_0x_0} + 1\right) = f\ln\frac{V}{V_0}$$

which can be solved for the salt content of the compacted suspension:

$$s = \frac{V_0x_0}{4}\left[\left(\frac{V}{V_0}\right)^{f} \mathrm{e}^{y} + \left(\frac{V}{V_0}\right)^{-f} \mathrm{e}^{-y} - 2\right] \tag{11}$$

where e = base of the natural logarithm and:

$$y = \operatorname{arccosh}\left(\frac{2\,s_0}{V_0x_0} + 1\right)$$

By differentiation of eq. 11 to V, the solution for $m_{\mathrm{Cl}}^{\mathrm{II}}$ is found:

$$m_{\mathrm{Cl}}^{\mathrm{II}} = \frac{\mathrm{d}s}{\mathrm{d}V} = \frac{f\,V_0 x_0}{4\,V} \left[\left(\frac{V}{V_0}\right)^{f} \mathrm{e}^{y} - \left(\frac{V}{V_0}\right)^{-f} \mathrm{e}^{-y}\right] \tag{12}$$

In Fig.2 eq. 11 is divided by V to give the concentration in the pore solution, and is compared with the experimental data given by von Engelhardt and Gaida (1963), and in Figs. 3 and 4 eq. 12 with data given by Bolt (1961b).

For the calculation the horizontal axis is re-calibrated with $V = 1$ at the initial suspension composition. The initial amount of colloidal charge (x_0, equiv./l) is calculated at this point either from the void ratio (= volume of water over volume of solids) assuming 1 cm^3 clay to have 2.7-mequiv. cation exchange capacity (CEC), or from L, the liquid content (in grams of water per gram of clay) with a CEC of 0.93 mequiv./g for montmorillonite and of 0.45 mequiv./g for illite.

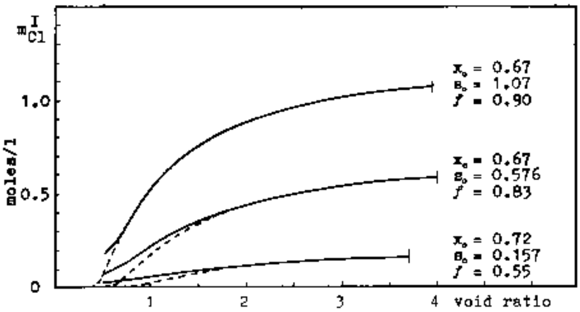

Fig. 2. Change of Cl$^-$ concentration in Na-montmorillonite suspensions during compaction. Dotted line, representing eq. 11 divided by V, is shown only where deviating from the solid line, experimentally found by von Engelhardt and Gaida (1963, fig. 12).

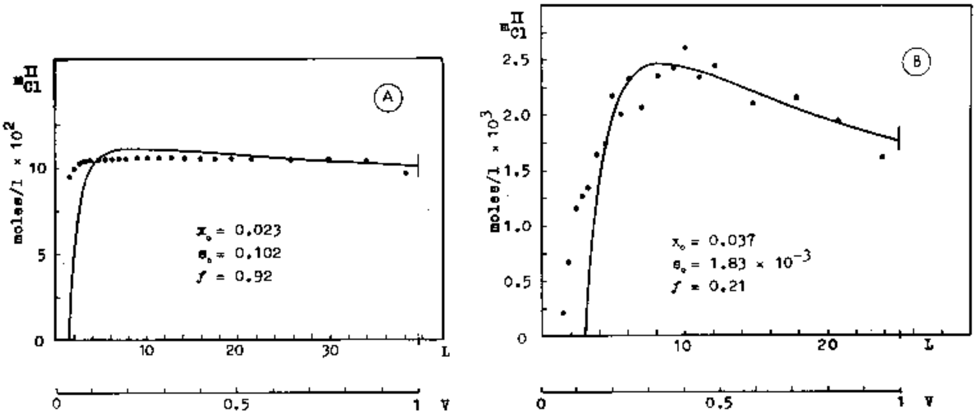

Fig. 3. Cl$^-$ concentration in water expelled from Na-montmorillonite, calculated with eq. 12.
Experimental points from Bolt (1961b, figs. 1 and 3).

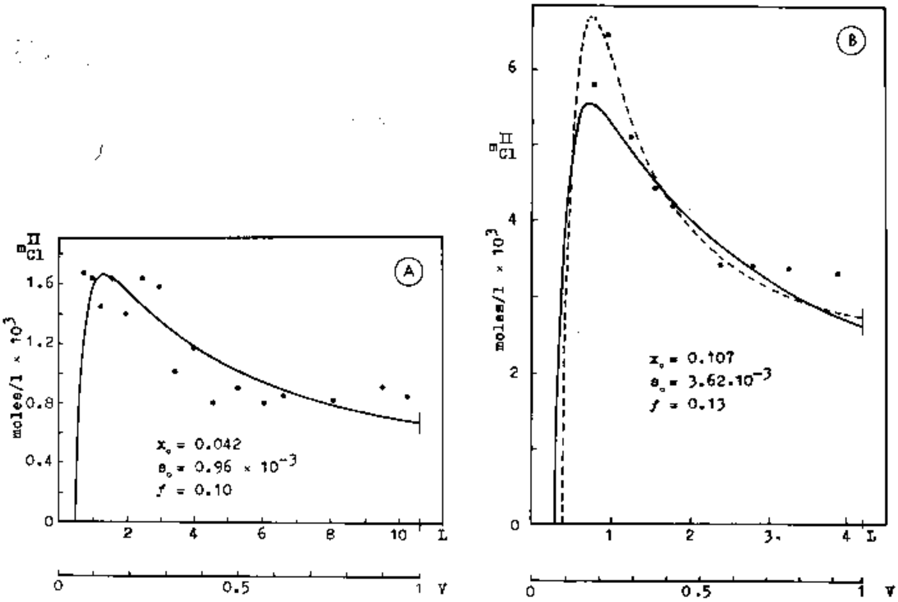

Fig. 4. Cl⁻ concentration in water expelled from Na-illite, calculated with eq. 12. Experimental points from Bolt (1961b, figs. 5 and 6). The dotted line in B is from Bolt, (1961b), calculated for the ideal suspension, but corrected for retention over the filter.

The best-fitting curves were selected from varying f. The agreement is good, in spite of the assumed constancy of f. This will be discussed later on.

ad (2): Mass-balance solution: $m_{\mathrm{Cl}}^{\mathrm{II}} = (s_0 - s)/(V_0 - V)$

Inserting the mass balance into eq. 9 and rearranging gives:

$$s^2\left[1-\left(\frac{f}{V}\right)^2(V_0-V)^2\right]+s\left[-2\,s_0-\left(\frac{f}{V}\right)^2 V_0x_0(V_0-V)^2\right]+s_0^2=0$$

This equation is readily solved to give the root:

$$s=\frac{1}{2\left[1-\left(\frac{f}{V}\right)^2(V_0-V)^2\right]}\left\{2\,s_0+\left(\frac{f}{V}\right)^2 V_0x_0(V_0-V)^2-\right.$$

$$\left.-\left[\left\{-2s_0-\left(\frac{f}{V}\right)^2 V_0x_0(V_0-V)^2\right\}^2-4\,s_0^2\left\{1-\left(\frac{f}{V}\right)^2(V_0-V)^2\right\}\right]^{1/2}\right\} \tag{13}$$

and the concentration in the suspension becomes a function of V:

$$m_{\mathrm{Cl}}^{\mathrm{I}} = \frac{s}{V} = \frac{(\mathrm{eq.}13)}{V} \tag{14}$$

The concentration outside the suspension becomes:

$$m_{\mathrm{Cl}}^{\mathrm{II}} = \frac{s_0 - s}{V_0 - V} = \frac{s_0 - (\mathrm{eq.}13)}{V_0 - V} \tag{15}$$

Eqs. 14 and 15 are depicted in Fig. 5. Again it is seen that the salt concentration in the suspension decreases upon compaction confirming equal reasoning by von Engelhardt and Gaida (1963) and Kryukov (1967), based on experiments.

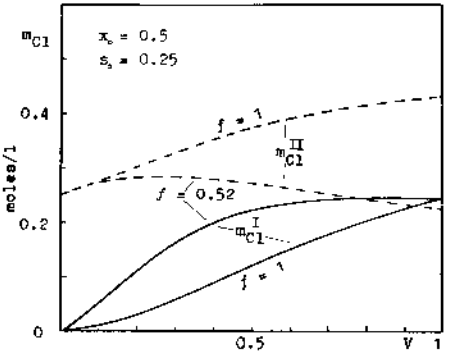

Fig. 5. The concentration of chloride inside (full line) and outside (dotted line) a compacting clay suspension based on mass balance.
Ideal behaviour is depicted with $f = 1$, whereas the actual ratio of activity coefficients is estimated from Fig. 6 to be $f = 0.52$.

DISCUSSION

It will be noted that during the mathematical manipulation f is kept constant, whereas it is a function of V presumably. To account for such changes presents a serious problem. Theoretically, it seems possible to calculate a $\gamma_{\pm}$ in the suspension from Gouij-Chapman theory, if the amount of overlapping of the double-layers is known (cf. Overbeek, 1956). From a more qualitative reasoning also, one would expect the activity coefficients in the suspension to be smaller than in the clear supernatant of the same ionic composition (i.e., $f < 1$). In Fig. 6, f, as found from the best-fitting curves in Figs. 2—4, is shown to be related to the ratio of the amount of colloidal charge over the original amount of chloride in the suspension.

From Fig. 6 one would judge that the change in f is low if $x_0/s_0 > \sim 20$, supporting the use of a constant f in that case. If $x_0/s_0 < \sim 20$, one would expect a lowering of f during the compaction, due to an increasing amount of colloidal charge and a decreasing salt concentration in the suspension. This would tend to suppress the negative adsorption still more, explaining perhaps the lack of agreement during the latter stage of compaction of montmorillonite in solutions with higher salt content (Figs. 2 and 3A). The lack of agreement may be caused also by hyperfiltration over the dense mat of clay minerals which is created during the compaction. Bolt, in fact, explained his results as due to hyperfiltration over the membrane filters which were used. His model gives good agreement where calculated (Fig. 4). It was not checked however, that the filters with adhering clay particles hyperfiltrated clear solutions of the same ionic composition.

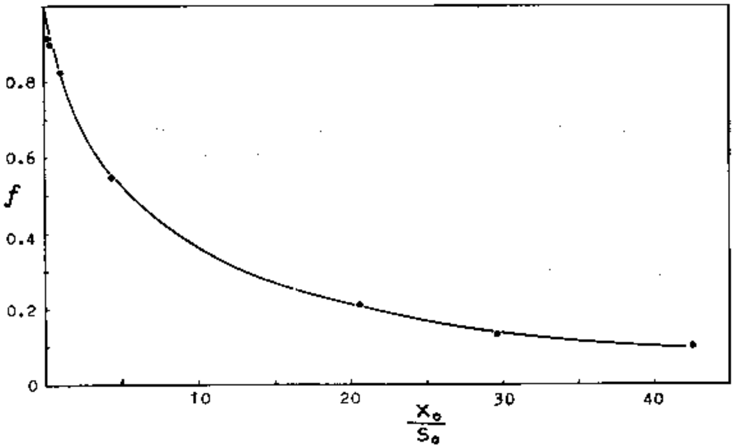

Fig. 6. The ratio of activity coefficients inside and outside a charged clay suspension, depending on the ratio of colloidal charge over ionic charge x_0/s_0.

SUMMARY AND CONCLUSIONS

Interpretation of the chemistry of solutions squeezed from clayey sediment samples in terms of original solute concentration in the sediment may be haphazard. The chemistry of the expelled solutions depends upon the electrolyte content of the solution, the concentration of charged colloidal material and the amount of compaction. Still more difficult is the interpretation in terms of activities; the ratio of the activity coefficients seems to be related to the ratio of colloidal charge over the amount of co-ions.

It seems quite clear however, that the ion concentration in suspensions of charged colloids decreases upon compaction. This conclusion bears upon compacting clay layers in physicochemical equilibrium with their surroundings as well.

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