DISCUSSION

DIFFUSION OF SEAWATER IONS: SIGNIFICANCE AND CONSEQUENCES OF CROSS COUPLING EFFECTS

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ABSTRACT. The cross coupling diffusion coefficients presented by Lasaga (1979) are critically appraised. It is shown that these parameters have a limited geochemical significance and can not be used to estimate the cross coupling diffusion fluxes in pore water of marine sediments. It is further shown that non-reacting ions in interstitial water of marine sediments should exhibit a stationary concentration gradient with depth with no net flux with respect to the sediment water interface.

INTRODUCTION

In a recent paper, Lasaga (1979) discussed the treatment of diffusion in a multicomponent system, such as seawater, and defined a parameter \( D_{ij} \) to characterize and quantify the diffusion of component \( i \) as a function of a concentration gradient in \( j \). The cross coupling parameter, as defined by Lasaga, is large for certain seawater ion couples, even approaching the value of the self diffusion coefficients of some ions. For example \( D^{\text{Na+Mg^{2+}}} \), which relates the diffusion of Na\(^+\) to a concentration gradient in Mg\(^{2+}\), is estimated to be \( 0.75 \times 10^{-5} \text{ cm}^2/\text{sec} \) as compared to \( D^{\text{Na+Na+}} = 1.546 \times 10^{-5} \text{ cm}^2/\text{sec} \) and \( D^{\text{Mg^{2+}Mg^{2+}}} = 0.898 \times 10^{-5} \text{ cm}^2/\text{sec} \). These estimated values of \( D_{ij} \) give the impression that a concentration gradient of one ion may result in large fluxes of other ions. This superficial impression is strengthened in the criticism made by Lasaga (1979) of the model calculation made in an earlier investigation (Ben-Yaakov, 1972). In that study, I demonstrated the applicability of a simple model to the diffusion of seawater ions and considered the possible effects of sulfate and bicarbonate diffusion, in anoxic marine sediments, on other pore water ions. It was assumed that only the ions involved in diagenetic processes are diffusing while the others, say Cl\(^-\), are stationary with respect to the sediment seawater interface. Lasaga criticized this assumption on the basis of his treatment of the cross coupling diffusion coefficients, \( D_{ij} \), and concludes that the diffusion of sulfate and bicarbonate must be accompanied by diffusion of other ions. I believe that this conclusion is incorrect and that the mathematical treatment of Lasaga (1979) reveals little if anything on the magnitude of ionic fluxes due to cross coupling.

The purpose of this note is to assess the significance of the cross coupling parameters \( D_{ij} \) as defined by Lasaga (1979), and to demonstrate that they are of limited geochemical significance. It will also be shown that the assumptions made earlier (Ben-Yaakov, 1972) are sound and that large cross coupling fluxes, as implied by Lasaga, probably do not prevail in marine sediments. It will be argued that cross coupling effects may cause stationary concentration gradients for non reacting ions.
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There are, however, no theoretical implications nor physical evidence that necessitate the assumption of continuous fluxes for ions that are not involved in a chemical reaction in the sediment.

For the sake of clarity, I shall confine the discussion to a model that takes into account diffusion cross coupling due to electrical interaction. The cross coupling effects due to ion pairing (Ben-Yaakov, 1972, 1973; Lasaga, 1979) have been studied recently (Katz and Ben-Yaakov, 1980), and it was found that they could be significant in geochemical systems. However, this theoretical refinement is not needed for the qualitative discussion presented here.

**FUNDAMENTAL RELATIONSHIPS**

Starting with the fundamental thermodynamic principles which relate the flux of species $i$ to the electrochemical potential and assuming electro-neutrality one obtains (Katz and Ben-Yaakov, 1980):

$$J_i = -D_i \frac{\partial C_i}{\partial x}$$  \hspace{1cm} (1)

where

$$D_i = D_i^\circ \left( 1 - \frac{Z_i FC_i}{RT} \frac{E}{\partial x} \right)$$  \hspace{1cm} (2)

$$D_i^\circ = u_i RT$$  \hspace{1cm} (3)

$$E = \frac{RT}{F} \sum_i Z_i u_i \frac{\partial C_i}{\partial x}$$  \hspace{1cm} (4)

and

$D_i$ = diffusion coefficient of species $i$

$D_i^\circ$ = self diffusion coefficient of species $i$

$J$ = flux (mole/cm²·sec)

$C$ = concentration (mole/cm³)

$u$ = mobility at infinite dilution (cm²·mole/J·sec)

$Z$ = valence

$F$ = Faraday's number (96,500 coulomb/eq)

$R$ = gas constant (8.3 J/deg·mole)

$E$ = electrical field (v/cm)

These relationships take into account the forces due to concentration gradients and electrical potential but neglect the electrophoretic and relaxation effects (Harned and Owen, 1958), neglect the variation of activity coefficients along the diffusion path, and neglect the ion pairing effect.

The magnitude of the electric field, $E$, expresses the amount of adjustment in the diffusion coefficients needed to ensure that the total charge, carried by the diffusing ions, is equal to zero — as required by the electroneutrality principle. As such, the numerical value of the
electric field is a measure of the mismatch between the self diffusion coefficients of the ions. This point is further illustrated by considering the dependence of $E$ on the other parameters of the system.

The usual method for deriving the explicit expression for $E$ is first to write (i) flux equations of the form (Ben-Yaakov, 1972):

$$ J_i = -u_i \left( RT \frac{\partial C_i}{\partial x} - Z_i F C_i E \right) $$  \hspace{1cm} (5)

and then to multiply these equations by $Z_i$

$$ Z_i J_i = -u_i \left( Z_i RT \frac{\partial C_i}{\partial x} - Z_i^2 F C_i E \right) $$  \hspace{1cm} (6)

The electroneutrality requirement is expressed as (Ben-Yaakov, 1972):

$$ \sum Z_i J_i = 0 $$  \hspace{1cm} (7)

Hence, the (i) equations of the form of eq (6) can now be summed up:

$$ \sum Z_i J_i = -RT \sum u_i Z_i \frac{\partial C_i}{\partial x} + F E \sum Z_i^2 C_i u_i = 0 $$  \hspace{1cm} (8)

From which eq (4) is readily obtained:

$$ E = \frac{RT}{F} \sum u_i Z_i \frac{\partial C_i}{\partial x} \quad \sum Z_i^2 C_i u_i $$  \hspace{1cm} (4)

This equation may give the impression that the electric field is a function of the concentration $C$ and concentration gradients $\partial C/\partial x$ of all ions. Such a conclusion, however, will be incorrect. The electric field is a function of the diffusing ions only (that is, for which $J_i \neq 0$) and independent of the stationary ions in solutions for which $J_i = 0$. This is easily seen by considering the set of eqs (8). One can exclude from the summation all the equations for which $J_i = 0$ that is

$$ E = \frac{RT}{F} \sum_{k=1}^{m} u_k Z_k \frac{\partial C_k}{\partial x} \sum_{k=1}^{m} Z_k^2 C_k u_k $$  \hspace{1cm} (9)

Eq (9) now includes only diffusing ions, that is:

$$ J_k \neq 0 \quad (k = 1, \ldots, m) $$  \hspace{1cm} (10)

it is important to note that zero flux does not necessarily imply a zero concentration gradient. This is inferred by considering again the basic flux equation for zero flux:

$$ J_i = -u_i \left( RT \frac{\partial C_i}{\partial x} - Z_i F C_i E \right) = 0 $$  \hspace{1cm} (11)
from which one derives the relationship between the concentration gradient and electric field for zero flux condition:

\[
\frac{\partial C_i}{\partial x} = \frac{FZ_i}{RT} E_i.
\]  

(12)

The concept of a stationary concentration gradient balanced by an electric force and resulting in a zero diffusion flux is not new and dates back to Nernst. This idea is fundamental to the theory of membrane electrodes (Hills, 1961) and specific ion electrodes (Durst, 1969). It will be argued below that one would expect a similar situation in anoxic marine sediments.

Cross diffusion coefficients.—Combining eqs (4) and (5):

\[
J_i = -u_i RT \frac{\partial C_i}{\partial x} + Z_i F C_i u_i \sum_k u_k Z_k \frac{\partial C_k}{\partial x} - \frac{Z_i Z_j u_i u_j F}{u_j Z_j C_j} \sum_k \frac{u_k Z_k C_k}{C_j} \frac{\partial C_k}{\partial x}.
\]  

(13)

which can be rewritten in the form:

\[
J_i = -D_{i \to} \frac{\partial C_i}{\partial x} - D_{ij} \frac{\partial C_j}{\partial x}
\]  

(14)

where

\[
D_{i \to} = RT u_i,
\]  

(3)

\[
D_{ij} \frac{\partial C_i}{\partial x} = \frac{C_i Z_i Z_j u_i u_j F}{u_j Z_j C_j} \sum_k \frac{u_k Z_k C_k}{C_j} \frac{\partial C_k}{\partial x} \quad (i \neq j)
\]  

(15)

The \( D_{ij} \) so defined conform to the Onsager reciprocal theory of irreversible thermodynamics which states that if the diffusion fluxes are written as a function of the chemical potential \( \mu_i \):

\[
J_i = \sum_j L_{ij} \frac{\partial \mu_i}{\partial x}
\]  

(16)

then

\[
L_{ij} = L_{ji}
\]  

(17)

This relationship is equivalent, in our case, to the equality:

\[
C_i D_{ij} \frac{\partial C_i}{\partial x} = C_j D_{ij} \frac{\partial C_j}{\partial x}
\]  

(18)

It is self evident that the definition of \( D_{ij} \) (eq 5) satisfies this reciprocal requirement.

Lasaga (1979) chose to define a different cross diffusing coefficient which was derived by using the electroneutrality relationship:

\[
-Z_i \frac{\partial C_i}{\partial x} = \sum_{j=1}^{n-1} Z_j \frac{\partial C_j}{\partial x}
\]  

(19)

He then defined a cross diffusion coefficient as

\[
D_{ij} = -\frac{Z_i C_i D_{i \to} (D_{j \to} Z_j - D_{ij \to} Z_j)}{\sum_k Z_k C_k D_{k \to}}
\]  

(20)
Although correct from the mathematical point of view, the $D_{ij}$ so defined have imbedded in them an erroneous physical assumption. The $D_{ij}$ so defined implicitly assume that the charge concentration increment due to a concentration gradient in all ions (i) other than Cl$^{-}$ is counter balanced by an equivalent charge concentration gradient (of opposite sign) of the chloride ion. Although this may be the situation in some special cases, this assumption is obviously wrong when deriving a general relationship. As a result of this intrinsic assumption, the $D_{ij}$ are a function of the difference between the infinite dilution mobilities of each ion and the chloride ion:

$$Z_i D_{i}^{o} - D_{Cl}^{o} Z_j = Z_j (D_{j}^{o} - D_{Cl}^{o}) = RT Z_j (u_j - u_{Cl}) \tag{21}$$

Consequently, the $D_{ij}$ for K$^+$ (that is, $D_{i,K^+}$) are very small because the mobilities of K$^+$ and Cl$^{-}$ are almost identical, whereas the $D_{ij}$ for Na$^+$ (that is, $D_{i,Na^+}$) are relatively large because there is a relatively large difference between $D_{i,Na^+}$ and $D_{Cl}^{o}$.

Considering the fact that the magnitude and sign of a given $D_{ij}$ is a function of the factor $-Z_i (D_{i}^{o} - D_{Cl}^{o})$, any attempt to attach physicochemical or geochemical significance to the magnitude or sign of the $D_{ij}$ in marine sediments is bound to be futile. For example, the statement (Lasaga 1979, p. 341): “In general, for the case of no ion pairing if $j$ refers to a negatively charged ion, $D_{ij}$ is positive for negative (i $\neq j$) ions (Coulomb repulsive forces increase motion), and $D_{ij}$ is negative for positive i ions (attraction reduces motion)” is clearly erroneous. Cross coupling diffusion coefficients have nothing to do with Coulomb attraction and repulsion forces but rather express the partial dependence of the diffusion flux of an ion i on the concentration gradient of an ion j. Consequently, $D_{ij}$ should be positive if the i and j ions have opposite charge polarities, because such ions must diffuse in the same direction to maintain electroneutrality — if the concentration gradients are of the same sign. However, $D_{Mg^{2+}, SO_{4}^{2-}}$, as defined by Lasaga is negative (Lasaga 1979, table 5) because $D_{SO_4^{2-}} < D_{Cl^{-}}$ (see eq 20 above) and not because "attraction reduces motion", as explained by Lasaga. Furthermore, since the definition of $D_{ij}$ is inconsistent with the principles of irreversible thermodynamics (Onager, 1981), they may lead to unacceptable conclusions. For example, the calculated values for $D_{Mg^{2+}, SO_{4}^{2-}}$ and $D_{SO_{4}^{2-}, Mg^{2+}}$ in seawater (including ion pairing effects) are: $0.131 \times 10^{-2}$ cm$^2$/sec and $-0.007 \times 10^{-2}$ cm$^2$/sec respectively (Lasaga, 1979, table 4). This implies that if SO$^{2-}$ and Mg$^{2+}$ have the same concentration gradients (and assuming that everything else is constant!) the sulfate and magnesium ion cross coupling diffusion will be in opposite directions. Such a conclusion is unacceptable because it violates the principle of microscopic reversibility which states (Harned and Owen, 1978; p. 119): “the flow of the $i^{th}$ species of ion under unit force per unit amount $k^{th}$ species equals the flow of the $k^{th}$ species under unit force of per unit quantity of the $i^{th}$ species.” The erroneous result is a direct consequence of the a priori assumption that the chloride ion counter-balances the electrical
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diffusion flux of all other ions — an assumption that is imbedded in
the definition of \( D_{ij} \). One can thus conclude only that the magnitude
and sign of the \( D_{ij} \) have little if any geochemical significance even
though they are consistent from the mathematical point of view.

Diffusion of non-reacting ions.—Lasaga (1979) criticized the assumption
made in an earlier work (Ben-Yaakov, 1972) concerning the diffusion
of major ions in pore water of anoxic marine sediments. The assump-
tion made was that the charge carried by the sulfate diffusion flux into
the sediment is balanced by the charge carried by the bicarbonate
flux out of the sediment, that is, that all other ions are stationary with
respect to the sediment-water interface (except for minor constituents,
which are by-products of the diagenetic processes). Using a diffusion and
reaction model presented earlier by Berner (1964) and Lasaga and
Holland (1976), Lasaga showed that the assumption of a charge flux
balance between sulfate and bicarbonate implies that

\[
2 D_{SO_4^{2-}} \frac{\partial SO_4^{2-}}{\partial x} = - D_{HCO_3^-} \frac{\partial HCO_3^-}{\partial x}
\]

(22)

which according to him is incorrect. He therefore concluded that other
ions must also move. There is, however, no reason why relationship (22)
should not hold in anoxic marine sediments. Recalling that the diffusion
coefficients are given by:

\[
D_i = D_i^c \left( 1 - \frac{Z_i F}{RT} \frac{C_i E}{\partial C_i / \partial x} \right)
\]

(2)

it is obvious that the diffusion coefficient of any given ion (i) is a func-
tion of the electric field \( E \) which, in turn, is a function of the self dif-
fusion coefficients mismatch between the diffusing ions only (eq 9). It is
thus evident that the case on hand is similar to the problem of diffusion
of a single salt. In both cases the diffusion coefficients are adjusted by
the field \( E \) so as to ensure a zero charge flux.

As discussed earlier (Ben-Yaakov, 1972), the onset of the electric
field \( E \) will force a concentration gradient for all other ions. It is, how-
ever, unreasonable to assume a continuous diffusion flux for ions not
involved in a chemical reaction in the sediment. It would be much more
reasonable to assume a short transient period during which the non-
reacting ions will assume a concentration gradient that is sufficient to
balance out the force due to the electric field. The magnitude of the
required concentration gradient is very small (Ben-Yaakov, 1972), much
below the present analytical precisions (the expected gradients are larger
if one takes into account the effect of ion pairing as discussed by Katz
and Ben-Yaakov, 1980).

It should be pointed out in this connection that the mathematical
treatment of the diffusion model (Lasaga and Holland, 1976) as presented
by Lasaga (1979, p. 344) is incorrect. The integration of the partial
differential equations was made under the assumption that \( D_{SO_4^{2-}} \) and
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$D_{\text{HCO}_3^-}$ are constant along the diffusion path. This is clearly incorrect in the general case since the bulk diffusion coefficient $D_i$ is a function of $E$, $C_i$, $\delta C_i/\delta x$ (eq 2) none of which can be assumed to be constant with depth. It may appear superficially, that the expected deviation of $D_i$ from $D_i^0$ will be quite small, if $i$ is a minor ion because $E$ (eq 4) is apparently small, and hence if $C_i$ is low $D_i \rightarrow D_i^0$ (eq 2). However, such a conclusion will be incorrect. As already shown above, the electric field $E$ is a function of the diffusing ions only (eq 9). Hence, if the ionic diffusion fluxes in the sediment are due mainly to the diffusion of $SO_4^{2-}$ and $HCO_3^-$ the magnitude of $E$ will be a function of these ions only (eq 9) as if all other ions were absent. Furthermore, examination of eq (2) reveals that the deviation of $D_i$ from $D_i^0$ is also a function of the ratio $C_i/(\delta C_i/\delta x)$ which could be large even if the concentration $C_i$ is low. It is thus evident that one cannot accept without rigorous proof the conjecture that $D_{\text{HCO}_3^-}$ and $D_{\text{SO}_4^-}$ are constant in an anoxic marine sediment.

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References


