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# Radiotracer Probing of Solute Transport at Solid/Solution Interfaces in Equilibrium Systems*

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In a system consisting of solid in equilibrium with its solution there is a bidirectional transfer of material (solute) across the solid/liquid interface. By means of radioactive tracers and using compartmental analysis the information can be obtained pertaining to the number of material transport routes in such a system and their extent as well as to the quantity of the herein participating material. The possibilities of this approach to the evaluation of solute transport at solid/solution interface are illustrated by utilizing the results of radiotracer studies of ion transport in two kinds of aqueous systems. One containing a single crystal of $CaF_2$ and the other being a suspension of crystalline particles of $CaSO_4 \cdot 2H_2O$.

## INTRODUCTION

In a system consisting of a solid immersed in a solution of this very solid there is a permanent transfer of solute from the solid into the solution and *vice versa*. In saturated solutions the rate of transfer (flow) of solute across the solid/solution interface is expected to be the same for both directions. No net transport but only the exchange of material between the two phases occurs and consequently the quantity of material in different parts of the system remains constant: the system is in a state of dynamic equilibrium or steady state.

A study of material transport at the interface in such a system should preferably comprise the determination of transport rates of the solute and its quantity in different parts of the system including the interface. For this purpose a radioactive tracer for the solute molecules or for one of its ions has to be added to the system and the quantity of tracer in one of the phases or parts of the system measured as a function of time.

In the past, the McKay equation (published in 1938)[1] and some others, similar equations were used to delineate the time curves for tracer. According to McKay (and his terminology) the kinetics of an isotopic exchange reaction:

$$AX^* + BX = AX + BX^*$$

where $X^*$ represents a labelled (for example, radioactive) X atom, could be described by equation:

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$$-\ln\left(1-\frac{x}{x_\infty}\right) = R\left(\frac{a+b}{ab}\right)t \qquad (1)$$

Herein $a$, $b$, and $x$ are the concentrations of respectively AX, BX and AX*, $R$ the exchange rate and $t$ is the time. This equation is valid if $a \gg x$, $x = 0$ when $t = 0$ and $x = x_\infty$ when $t = \infty$.

Equation (1) enables the determination of the exchange (transport) rate in systems with only one exchange path. Nevertheless it was not seldom applied for the evaluation of tracer behaviour in the systems with more than one exchange path. The thus reached conclusions regarding the material exchange in such systems are not always entirely convincing.

A more proper and straightforward elaboration of the data acquired by the tracer experiments in systems consisting of a solid phase and a corresponding solution can be achieved by means of the compartmental analysis resulting in a model of the system being studied. This approach — very well known and widely applied in life sciences[2,3] — has hardly ever been utilized in the radiotracer studies of transport processes at the solid/solution interface.

## COMPARTMENTAL ANALYSIS

A compartmental system is a system made up of a finite number of subsystems or compartments each of which is homogeneous and well mixed, and wherein the compartments interact by exchanging material. If there are no exchanges of material with the environment, the system is said to be closed. A compartment is also an amount of a material which acts kinetically like a distinct, homogeneous, chemically or physically identical amount of the material. Moreover a compartment is a chemical or physical subdivision of a system, through which the ratio of concentration of tracer to tracee (material being traced) is uniform at any given time.[4] This ratio is usually called the specific activity and may be expressed as Bq · mol$^{-1}$.

A model of a system in which solute material is being exchanged between a solution and a solid phase should comprise at least two compartments (a and b in Figure 1).

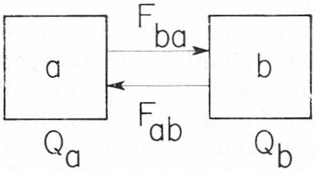

Figure 1. A model of a closed two compartment system. $Q$ is the quantity of material in a compartment and $F$ the rate of transfer (flow) of material.

The quantity of material in a compartment is $Q$ mol (e. g. $Q_a$ is the quantity in compartment a). There is a flow of material with rate of transfer to compartment b from a, $F_{ba}$ mol · s$^{-1}$ and to compartment a from b, $F_{ab}$ mol · s$^{-1}$. The rate constant for the transfer from compartment a and b are respectively $k_{ba} = F_{ba}/Q_a$ and $k_{ab} = F_{ab}/Q_b$ s$^{-1}$. If the system contains a radioactive tracer then the rate of change of quantity of tracer $q(t)$ Bq in any compartment is determined by the rates of acquisition and rates of loss of tracer. The differential equations describing this for compartment a and b are therefore:

$$dq_a(t)/dt = k_{ab}\, q_b(t) - k_{ba}\, q_a(t) \tag{2}$$

$$dq_b(t)/dt = k_{ba}\, q_a(t) - k_{ab}\, q_b(t) \tag{3}$$

The solutions of the equations (2) and (3) are of the following exponential form when expressed in terms of fraction of the tracer amount $q_a(0)$ Bq introduced in compartment a at zero time:

$$q_a(t)/q_a(0) = H_1\, e^{-g_1 t} + H_2 \tag{4}$$

$$q_b(t)/q_a(0) = K_1\, e^{-g_1 t} + K_2 \tag{5}$$

Thus, the curves consist of one exponential term plus a constant. In the equations (4) and (5) $g_1 = k_{ba} + k_{ab}$, $H_1 = k_{ba}/g_1$, $H_2 = 1 - H_1 = k_{ab}/g_1$, $K_1 = -k_{ba}/g_1$ and $K_2 = k_{ba}/g_1$.

Frequently the number of compartments comprising a system is not known *a priori* and the evaluation of the time course of the change of the tracer amount in one ore more compartments has to include an estimation of that number. The usual approach to this is to determine the number of exponential terms necessary to delineate the $q(t)/q_a(0)$ versus time curve hence the number of compartments and the number of exponential terms (of which one perhaps with $g = 0$) are essentially the same. The following step in the compartmental analysis is setting up a model and the estimation of the system parameters (e. g. quantity of material in each compartment and the rate of material transfer between them).

## ELABORATION

The possibilities of the »compartmental« approach to the evaluation of the solute behaviour at solid/solution interface will be illustrated by using the results of radiotracer studies of two systems each consisting of a sparingly soluble calcium salt and a saturated aqueous solution of the respective salt.

### 1. *Calcium Transport in a $CaF_2$-based System*[5,6]

This system was obtained by equilibration with water (at 25 °C) of a single crystal (in the form of a regular pyramid with 4 sides of about 20 mm and the slant height of 18 mm) of the mineral fluorite ($CaF_2$). After the equilibration the crystal was removed from the (saturated) solution and $q_a(0)$ Bq of $^{45}Ca^{2+}$ (radiotracer for $Ca^{2+}$) was added to it. The activity (tracer amount) present at an area $A$ ($= 10^{-5}$) m$^2$ of the crystal surface was measured at different crystal faces by means of a Geiger-Müller counter. After a few hundred hours (total immersion time $t$) the activity $q_f(t)$ Bq per $A$ m$^2$ at each of the crystal faces reached its maximal (constant) value $q_f(\infty)$.

The experimental data expressed as $q_f(t)/q_f(\infty)$ versus time $t$ fit to the equation having a general form:

$$q_f(t)/q_f(\infty) = K_1\, e^{-g_1 t} + K_2\, e^{-g_2 t} + 1 \tag{6}$$

and thus indicating the presence of at least three different calcium compartments; one of which being calcium in the solution and two others pertaining a crystal face of a certain type (e. g. [100] or [111]). If the mentioned three compartments are arranged according to Figure 2 and if $Q_b \ll Q_a \gg Q_c$ which is reasonable to assume because the quantity of calcium in the saturated solution of $CaF_2$ significantly exceeds that present at the crystal/solution interface (crystal surface), one can calculate some of the transport parameters of the system by making use of the following relations:

$$g_1 = k_{ba} + k_{ab} \doteq k_{ab} = F_{ab}/Q_b = 1/\bar{t}_b \tag{7}$$

$$g_2 = k_{ca} + k_{ac} \doteq k_{ac} = F_{ac}/Q_c = 1/\bar{t}_c \tag{8}$$

in which $\bar{t}_b$ and $\bar{t}_c$ are the mean residence times of calcium at the crystal/ /solution interface (thus pertaining to two different binding sites of calcium at one crystal face).

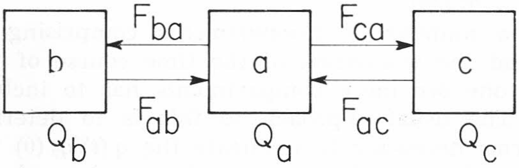

Figure 2. A model of a closed three compartment system with a central (solution) compartment.

The quantity of calcium $(Q_b + Q_c)/A$ participating in the transport processes occuring at the crystal/solution interface (»exchangable calcium«) may be calculated by means of the relation:

$$\frac{q_f(\infty)/A}{(Q_b + Q_c)/A} = \frac{q_a(\infty)}{Q_a} = \frac{q_a(0)}{Q_a} \tag{9}$$

where $(Q_b + Q_c)/A$ has the dimension of mol · m$^{-2}$.

A compilation of some of the typical results is given in Table I.

TABLE I

*Compilation of Some Data Pertaining to the Calcium Transport Across the Solid/Solution Interface in the System $CaF_2$-crystal/Aqueous Solution of $CaF_2$*+

| | | Crystal face | |
|---|---|---|---|
| | | [100] | [111] |
| $g_1/s^{-1}$ | | $1.5 \times 10^{-5}$ | $1.7 \times 10^{-5}$ |
| $g_2/s^{-1}$ | | $5.8 \times 10^{-7}$ | $6.7 \times 10^{-7}$ |
| $\bar{t}_b/s$ | | $6.7 \times 10^{4}$ | $5.9 \times 10^{4}$ |
| $\bar{t}_c/s$ | | $1.7 \times 10^{6}$ | $1.5 \times 10^{6}$ |
| $[(Q_b + Q_c)/A]/$ mol · m$^{-2}$ | Experiment (E) | $3.5 \times 10^{-14}$ | $4.0 \times 10^{-14}$ |
| | Theory (T)* | $5.6 \times 10^{-14}$ | $4.3 \times 10^{-14}$ |
| | (E)/(T) | 0.63 | 0.93 |

+ See the text for the exact meaning of the symbols.

* Calculated from crystallographic data.

### 2. *Calcium and Sulfate Ion Transport in $CaSO_4 \cdot 2H_2O$ (Gypsum) Based Systems*

This system was obtained by aging the suspensions consisting of $CaSO_4 \cdot 2H_2O$ crystals (particles) and a saturated aqueous solution of $CaSO_4$. At the beginning of an experiment $q_a(0)$ Bq of $^{45}Ca^{2+}$ or $^{35}SO_4^{2-}$ as tracers for respectively $Ca^{2+}$ and $SO_4^{2-}$ were added to a well agitated suspension which was then regularly sampled for at least $6 \times 10^5$ s (about 170 hours). Each sample has been filtrated in order to obtain clear solution and the quantity of tracer in the solution $q_a(t)$ was subsequently measured by means of liquid scintillation counting. The results of the measurements expressed as $q_a(t)/q_a(0)$ versus time are for three different aging times shown in Figure 3.

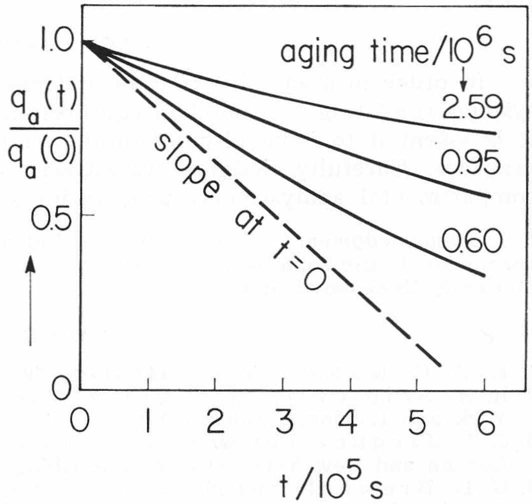

Figure 3. Fraction of the initial tracer amount in the solution compartment as a function of the elapsed time.

In the very first instant after zero time the only movement of tracer is of the solution (out of compartment a). None is returning from the other compartments, because none as yet exists outside compartment a. Consequently the rate constant $k_{aa}$ (sum of all rate constants of output from compartment a) is numerically identical with instantaneous slope of the $q_a(t)/q_a(0)$ versus $t$ curve (slope at $t = 0$ s). (See Figure 3). In the present system it means that:

$$\frac{d\,[q_a(t)/q_a(0)]}{dt} = k_{aa} = F_{cr,\,a}/Q_a \tag{10}$$

where $F_{cr,a}$ is the rate of transfer (flow) of calcium or sulfate ions to the crystals from the solution and $Q_a$ is the quantity of either calcium or sulfate ions in the solution. The $F_{cr,a}$ divided by the total surface area of the $CaSO_4 \cdot 2H_2O$ crystals present in the system (suspension) represents the flux of either of the ions and has the dimension mol $\cdot$ s$^{-1}$ $\cdot$ m$^{-2}$. (Table II).

The thus calculated flux values appeared to be independent on the type of the ion but clearly dependent on the aging time of the suspension. The

TABLE II

*Flux (= Flow per Unit Surface Area) of $Ca^{2+}$ and $SO_4^{2-}$ Ions at the $CaSO_4 \cdot 2H_2O$/ Solution Interface. Direction of the Flux: to Crystals From the Solution*

| *Aging time*/s | *Flux*/mol · $s^{-1}$ · $m^{-2}$ |
|---|---|
| $0.60 \times 10^6$ | $4.1 \times 10^{-10}$ |
| $0.95 \times 10^6$ | $2.7 \times 10^{-10}$ |
| $2.59 \times 10^6$ | $1.5 \times 10^{-10}$ |

decrease of the rate of material transfer at the interface with the duration of the aging indicates that the even after up to $0.95 \times 10^6$ s (264 hours) the system has probably not reached the state of dynamic equilibrium (steady state).

## CONCLUSION

In order to study the kinetics and mechanism of interfacial processes in systems consisting of a solid in equilibrium with a solution of this very solid it is essential to have disposal of data related to material transport at the interface. Carefully designed radiotracer experiments in combination with compartmental analysis may provide for such data.

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## SAŽETAK

### Ispitivanje prijenosa otopljenih tvari na granici faza čvrsto/otopina u ravnotežnim sustavima pomoću radioaktivnih obilježivača

*Z. Kolar*

U sustavu koji se sastoji od krutine u ravnoteži s otopinom postoji dvosmjerni transfer materijala (otopljene tvari) putem međupovršine čvrsto/tekuće. S pomoću radioaktivnih obilježivača (tracera) i upotrebom analize odjeljaka mogu se dobiti informacije o broju putova za transport materijala u takvim sustavima, njihovom opsegu kao i o količini materijala koji u tomu sudjeluje. Mogućnosti takvog pristupa u evaluaciji transporta otopljene tvari preko međupovršine čvrsto/tekuće prikazane su proučavanjem transporta iona u dvije vrste vodenih sustava. Jedan od njih sadrži pojedinačni kristal $CaF_2$, a drugi je suspenzija kristalnih čestica $CaSO_4 \cdot 2H_2O$.