# A Radiotracer Study of Cadmium Transport Across the CdS/Aqueous Solution Interface*

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Information on interfacial mass transport of cadmium in cadmium sulfide suspensions under equilibrium conditions has been obtained by probing with a radiotracer for cadmium. The transport of $Cd^{2+}$ ions from the cadmium sulfide solid particles to the saturated solution and visa versa is followed by adding radioactive $^{109}Cd^{2+}$ to the solution and measuring the amount of radioactivity present in the solution as a function of time. The amount of exchangeable cadmium in or at the solid/liquid interface, which is deduced from the final value of radioactivity in the solution appeared to be 1.8 to 2.3 times the amount of cadmium in one lattice layer.

Compartmental analysis of the experimental data revealed that 4 different cadmium species are involved in the exchange processes, one of which being the cadmium in the bulk of the solution, and another one, representing 40% to 50% of one lattice layer, which exchanges rapidly with the solution in comparison with the other two species left.

## INTRODUCTION

Systems consisting of CdS and an aqueous solution (e. g. CdS suspensions or colloids) have acquired much interest in recent years in variuous fields such as waste water treatment,[1] environmental research,[2] biotechnology[3] and photo-assisted water splitting.[4-6] An important and common aspect in all these areas is the transport of cadmium across the CdS/aqueous solution interface which may be either desired or undesired. CdS is one of the most promising semiconductor materials for water splitting, but it is also highly susceptible to corrosion.[7]

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As first part of our research pertaining to the CdS/aqueous solution systems we studied the solubility of CdS in water in the pH range 1 to 14.[8] In the present article we report on the transport of cadmium across the CdS/aqueous solution interface under steady state (equilibrium) conditions in the dark. In a forthcoming study the influence of illumination will be included.

The transport of cadmium at the CdS/aqueous solution interface in equilibrated, unilluminated suspensions of CdS is followed with the aid of the radiotracer technique using $^{109}Cd^{2+}$ as radiotracer. In the past the radiotracer technique was often used in suspension systems for determing the specific surface area of the particles in suspensions.[9-11] Recently it was shown at our laboratory that the radiotracer studies can also yield information on the transport mechanisms at the molecular level for the $CaF_2$ crystal/aqueous solution systems.[12] This was accomplished by a careful examination of the tracer system interrelations (tracer kinetics) followed by an interpretation of the system behaviour in terms of elementary transport processes (e. g. diffusion in the liquid or solid, adsorption and desorption).

## EXPERIMENTAL

Cadmium sulfide suspensions were prepared by adding precipitates, obtained by passing $H_2S$ gas through a solution, containing $5 \cdot 10^{-2}$ M $CdCl_2$ and 0.1 M $HNO_3$, to 0.5 $dm^3$ of a diluted $H_2SO_4$ (pH = 2) solution (type A). Further details of the precipitation procedure have been given elsewhere.[8] Also commercial CdS powder was used for preparing the suspensions (type B).

The CdS suspensions were equilibrated in the dark at 25 °C and pH = 2 prior to the exchange experiment, which was started by adding the tracer ion $^{109}Cd^{2+}$ in the form of a few microliters of a $^{109}CdCl_2$ solution ($3.9 \cdot 10^{-6}$ mol $\cdot$ $dm^{-3}$ Cd). After various time intervals aliquots were withdrawn from the suspensions. These aliquots were filtrated (pore size 0.025 μm) and the radioactivity of the filtrate was determined by means of liquid scintillation counting (LSC).

The specific surface area of the powders, used for preparing the suspensions, was measured by nitrogen adsorption according to the BET method. Atomic Absorption Spectroscopy was used for determining the amount of cadmium in the solution.

## RESULTS

In Figure 1, the relative radioactivity in the solutions is shown as a function of time for a suspension, containing 34.8 mg »own« CdS (type A). The tracer amount in the solution decreases asymptotically to about 40⁰/₀ of its initial value in this case. From the final value of the radioactivity in the liquid phase the amount of exchangeable cadmium in the system can be evaluated. At known solubility this means that the amount of exchangeable cadmium in or at the solid phase ($Q_s$) can be determined via:

$$Q_s = Q_T - Q_a \tag{1}$$

where $Q_T$ is the total amount of exchangeable cadmium in the system and $Q_a$ the amount of exchangeable cadmium in the solution, which is given by the cadmium concentration (the solubility at the pH of the experiment) and the volume of the solution. At $t = \infty$ all exchangeable cadmium in the system has the same specific activity. This leads to the relation:

$$q_a(\infty)/Q_a = q_a(0)/Q_T \tag{2}$$

where $q_a(0)$ and $q_a(\infty)$ are respectively the tracer amount, in the solution at $t = 0$ and $t = \infty$. Together with eq. (1) this gives for $Q_s$:

$$Q_s = [(q_a(\infty)/q_a(0))^{-1} - 1] \, Q_a \tag{3}$$

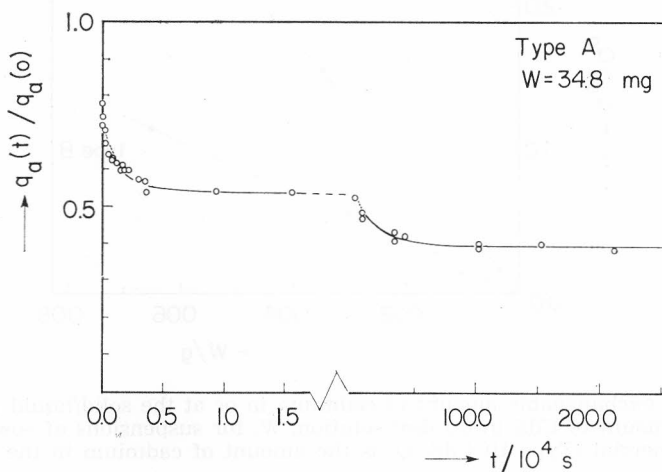For the system of Figure 1 we find now: $Q_s = 1.5 \, Q_a$.



Figure 1. The relative radioactivity in the solution, $q_a(t)/q_a(0)$, as a function of time for a CdS suspension of type A, containing 34.8 mg CdS in 0.5 dm³ solution.

In Figure 2, $Q_s/Q_a$ is plotted as a function of the amount of CdS (W) present in the system for both type A and type B suspensions. In both cases a linear dependence of $Q_s/Q_a$ on $W$ is found. The difference in slope, $d(Q_s/Q_a)/dW$, between the suspensions of type A and type B (Table I) can largely be explained on the basis of their respective specific surface areas as determined by the BET method. The value of $Q_s/Q_a$ per unit surface area is calculated by dividing the slope of the $Q_s/Q_a$ versus $W$ line by the specific surface area (Table I). The absolute value of $Q_s$ can now be calculated if $Q_a$, and therefore the solubility of the used CdS at pH = 2, is known. The cadmium concentration in the solution of the suspension after two weeks equilibrating was determined by Atomic Absorption Spectroscopy and amounts to: $1.35 \cdot 10^{-5}$ mol dm⁻³. This value is lower than was found previously, when a different CdS powder was used,[8] bit it is still lying within the 95⁰/₀ confidence interval. If $Q_a$ is calculated from this value for the solubility and the value for the volume of the solution ($V = 0.5$ dm³), $Q_s$ per unit surface area, $d(Q_s)/dA$, is calculated for the CdS suspensions of Type A and Type B to be respectively $2.25 \cdot 10^{-5}$ mol m⁻² and $2.81 \cdot 10^{-5}$ mol m⁻². These values can be compared with the amount of cadmium in one lattice layer, $Q_l$. The latter is calculated from the molecular weight, $M$, and the density, $\rho$, of CdS and the Alvogadro's number, $N_{av}$, according to:

$$Q_l = (N_{av})^{-1/3} \cdot (M/\varrho)^{-2/3} = 1.22 \cdot 10^{-5} \text{ mol m}^{-2}$$

This means that the amount of exchangeable cadmium in or at the solid/liquid interface equals 1.8 to 2.3 times the amount of cadmium in one lattice layer.
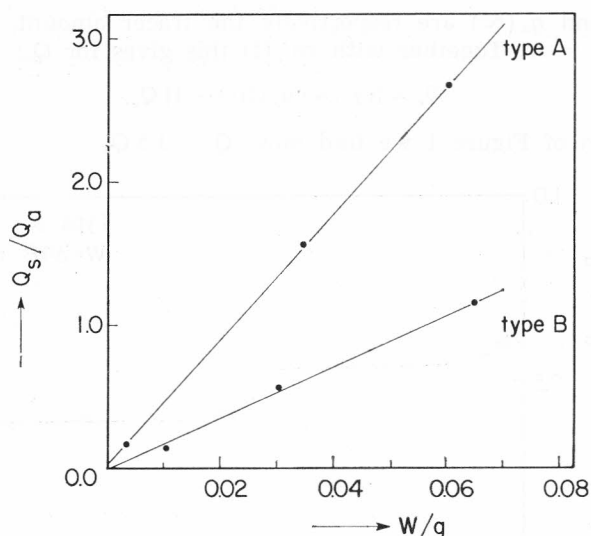
**Figure 2.** The exchangeable amount of cadmium in or at the solid/liquid interface, $Q_s$, against the amount of CdS in 0.5 dm³ solution, $W$, for suspensions of »own« (Type A) and commercial (Type B) CdS. $Q_a$ is the amount of cadmium in the solution.

TABLE I

*The Exchangeable Cadmium in or at the Solid/Liquid Interface for two Types of CdS Suspensions (See Text)\**

|  |  | Type A | Type B |
|---|---|---|---|
| $d(Q_s/Q_a)/dW$ | /g⁻¹ | 44.07 (0.51) | 17.93 (0.60) |
| $A_{BET}$ | /m² g⁻¹ | 13.20 | 4.31 |
| $d(Q_s/Q_a)/dA$ | /m⁻² | 3.34 (0.04) | 4.16 (0.14) |

\* $Q_a$ and $Q_s$ are the amount of exchangeable cadmium in respectively the solution and the surface of CdS. $A$ and $A_{BET}$ are respectively the total and specific surface area of the solid particles. Standard deviations are given in parentheses.

DISCUSSION

In the preceding section the total amount of cadmium, which is involved in the exchange process, is determined from the final value of the tracer amount in the solution.

Next the tracer behaviour is used to deduce the number of different cadmium species, involved in the exchange process. Therefore a compartment analysis is used, which is based on the assumption that specific compartments can be identified and that discharge of tracer therefrom can be described by exponential equations.[13,14] A compartment represents an amount of substance with a uniform distribution of tracer. In the present system one of

the compartments is made up by the cadmium in the solution. Other compartments may be formed by cadmium at various positions in the solid, adsorbed on the surface or in a boundary layer around the particles.

For a closed, steady state system, the tracer amount in the solution as a function of time can be described by:

$$q_a(t)/q_a(0) = H_n + \sum_{i=1}^{n-1} H_i \exp(-g_i t) \tag{4}$$

where $n$ is the number of compartments which are involved in the exchange and $H_i$ and $g_i$ are constants, which are related in a complicated way to the rate constants $k$ for the transport between the various compartments and their sizes $Q$ (the amount of exchangeable cadmium in the compartment).

It appears that at least three different exponential terms are necessary in order to obtain a proper fit to the experimental data. The sum of squares of deviations, divided by the number of degrees of freedom, has its minimum at $n = 4$. This means that four compartments are involved in the exchange process, one of which being the solution compartment.

The rate constants are giving the relations between fluxes and compartment sizes. The efflux from the solution, $F_{aa}$, is related to $Q_a$ as follows:

$$F_{aa} = k_{aa} Q_a \tag{5}$$

with:

$$k_{aa} = -\frac{d}{dt}[(q_a(t)/q_a(0))]_{t=0} = \sum_{i=1}^{3} H_i g_i \tag{6}$$

The rate constant of efflux from the solution, $k_{aa}$ (i. e. the sum of all rate constants of output from compartment »a«) per unit surface area for both types of CdS suspensions are presented in Table II. The large standard deviations, which are given in parentheses in this table, can be explained by the lack of experimental data in the initial part of the curve, because, according to eq. 6, $k_{aa}$ is based on the data in this part. Therefore the values of $d(k_{aa})/dA$, given in Table II, should be interpreted as the lower limits. Using eq. 5, the efflux per unit surface area, $d(F_{aa})/dA$, is calculated to be $\geq 0.3 \cdot 10^{-6}$ mol s$^{-1}$ m$^{-2}$ for type A, and $\geq 0.4 \cdot 10^{-6}$ mol s$^{-1}$ m$^{-2}$ for type B suspension.

TABLE II

*Cadmium Transport from the Solution†*

|  |  | Type A | Type B |
|---|---|---|---|
| $d(k_{aa})/dA$ | /s$^{-1}$ m$^{-2}$ | $\geqslant 0.041$ (0.017) | $\geqslant 0.059$ (0.013) |
| $d(Q_b/Q_a)/dA$ | /m$^{-2}$ | 0.76 (0.01) | 0.92 (0.04) |

† The rate constant for the cadmium transport from the solution to other compartments per unit surface area, $d(k_{aa})/dA$, and the ratio of the size of (amount of cadmium in) compartment $b$ and $a$ (solution) per unit surface area, $d(Q_b/Q_a)/dA$, for two types of CdS suspensions (see text). The standard deviations are given in parentheses.

It appears that the time constant of the first exponent in eq. 4, $g_1$, is much larger ($> 100$ times) than the other $g$ values. By approximation eq. 4 can be changed for $g_2 = g_3 = 0$ into:

$$q_a (t)/q_a (0) = \sum_{i=2}^{4} H_i + H_1 \exp (- g_1 t) \tag{7}$$

In that case the system can be described in the first part of the exchange process by a two compartment model, in which compartment »a« and »b« represent respectively cadmium in the solution and a relative fast exchanging cadmium species in or at the solid/liquid interface. Then we can write because of the condition of steady state:

$$F_{aa} = F_{ba} = F_{ab} = k_{ba}Q_a = k_{ab}Q_b \tag{8}$$

with:

$$k_{ba} = H_1 g_1 \quad \text{and} \quad k_{ab} = g_1 \sum_{i=2}^{4} H_i \tag{9}$$

where $k_{ba}$ and $k_{ab}$ are the constants for respectively the transport rates from compartment »a« to »b« and *visa versa*. Combining eq. 8 and eq. 9 leads to:

$$Q_b/Q_a = k_{ba}/k_{ab} = H_1/ \sum_{i=2}^{4} H_i \tag{10}$$

In Figure 3, $Q_b/Q_a$ is plotted as a function of the amount of CdS, $W$, for both type A and Type B suspensions. As was found for $Q_s/Q_a$, a linear dependency of $Q_b/Q_a$ on $W$ is found for both types of suspensions. The values for $Q_b/Q_a$ per unit surface area, calculated from the slope of the $Q_b/Q_a$ versus $W$ lines in Figure 3 and the specific surface areas, are pre-
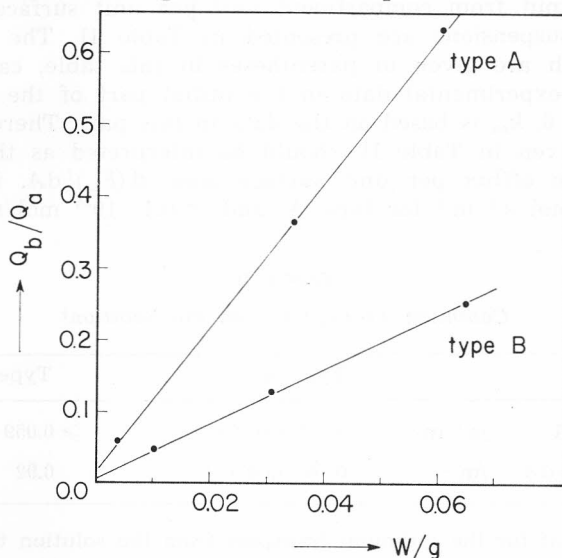


Figure 3. The size of compartment b (one of the three compartments in or at the solid/liquid interface), $Q_b$, against the amount of CdS in 0.5 dm$^3$ solution, $W$, for suspensions of »own« (Type A) and commercial (Type B) CdS. $Q_a$ is the amount of cadmium in the solution.

sented in Table II. The low value for the standard deviation (given in parentheses) for $d(Q_b/Q_a)/dA$ and $d(Q_s/Q_a)/dA$ indicate that the relative high standard deviation values of $k_{aa}$ originate from the large uncertainties, obtained for the $g_1$ values. If the solubility of CdS is $1.35 \cdot 10^{-5}$ mol dm$^{-3}$, $d(Q_b)/dA$ is calculated for the suspension of type A and type B to be respectively: $0.52 \cdot 10^{-5}$ mol m$^{-2}$ and $0.62 \cdot 10^{-5}$ mol m$^{-2}$.

It may be concluded, that, although the amount of exchangeable cadmium in or at the solid/liquid interface, $Q_s$, exceeds the cadmium amount in one lattice layer, the amount of the fast exchanging cadmium species, $Q_b$, includes only 40% to 50% of one lattic layer.

The evaluation of rate constants for the transport between the respective compartments, and their sizes (i.e. the amount of cadmium in the compartment) from the compartment analysis can contribute to the identification of these compartments or cadmium species and is carried on in detail at present. Additional experiments, where important parameters as e.g. temperature and cadmium concentration in the solution are varied, will be indispensable for a definite identification of all cadmium species.

## CONCLUSIONS

With the aid of the tracer experiments a characterisation of CdS/ /aqueous solution (suspension) system in terms of interfacial mass transport parameters could be performed.

In the present study the amount of exchangeable cadmium in or at the solid/liquid interface was determined to be 1.8 to 2.3 times the amount of cadmium in one lattice layer. In addition, it was found that 4 different cadmium species are involved in the exchange processes, one of which being the cadmium in the bulk of the solution, and another one representing 40% to 50% of one lattice layer, which exchanges rapidly with the solution in comparison with the other two species left.

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## SAŽETAK

### Proučavanje prijenosa Cd preko granice faza CdS/vodena otopina pomoću radioaktivnih obilježivača

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Ispitan je transport mase preko međupovršine kadmija u kadmij-sulfidu kod ravnotežnih uvjeta, s pomoću radioaktivnih obilježivača. Transport iona $Cd^{2+}$ iz krutih čestica kadmij-sulfida u zasićenu otopinu i obrnuto praćen je dodavanjem radioaktivnog $^{109}Cd^{+2}$ u otopinu i mjerenjem promjene količine radioaktivnosti u otopini s vremenom. Količina izmjenljivog kadmija u međupovršini čvrsto/tekuće, koja se izvodi iz konačne vrijednosti za radioaktivnost u otopini veća je 1,8 do 2,3 puta od količine kadmija u jednom monosloju (kristalne rešetke).

Analiza eksperimentalnih rezultata pokazuje da 4 različite kadmijeve vrste sudjeluju u procesu izmjenjivanja. Jedna je od njih kadmij u »bulk«-otopini, a drugu čini 40% do 50% jednog monosloja u kristalnoj rešetki koji se brzo izmjenjuje s otopinom u usporedbi s ostale dvije vrste.