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**A MECHANISTIC MODEL FOR COLLISIONAL DESORPTION**

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# A Mechanistic Model for Collisional Desorption

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## Abstract

A model is constructed for DiToro's proposal that particle-particle collisions may be responsible for decreased sorption at high particle concentrations. The basis of the model is that collisions between particles deposits energy at the particle surface which desorbs a small fraction of solute. At high particle levels, the displaced material is unable to fully resorb before the subsequent collision. The model also recognizes that collisional energy transfer is most efficient between particles of equal mass, and that two particles will collide many times on average before they fully separate. The equation resulting from the model reduces to a form equivalent to DiToro's empirical equation.

## Introduction

Solute partitioning between solids and water decreases with increasing solids concentration at high levels of solids (1-10). DiToro and others (1-4) have proposed that particle-particle collisions lead to increased desorption, and have developed an empirical equation that accommodates the data quite well. Others have invoked a "third phase" which is assumed to separate from the solids and associate with solute (7-9). Since this material is included in the aqueous phase, it lowers the apparent distribution coefficient.

There is ample evidence that third phase arguments apply to many situations where sorption is lower than expected (11). However, in an elegant series of experiments, DiToro factored out third phase effects and demonstrated that they cannot completely account for decreased sorption in all cases (2). He also demonstrated the phenomenon with glass beads where third phase effects are unlikely (12). In this paper we provide a mechanism and thermodynamic support for the collisional model, and validate DiToro's empirical equation.

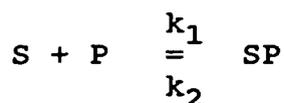
## Model Development

When two particles collide, kinetic energy is deposited at the particle surface. Einstein has shown that the particles involved have surprisingly high mean velocities through Brownian motion; for instance, the mean velocity of a 2.5 femtogram platinum particle in water at 19°C is 8.6 cm/sec (13). The mean displacement, however, is smaller by four orders of magnitude,

since the motion of the particle is random. It follows that two particles must, on average, collide many times through rotational and translational Brownian motion before they fully separate.

The energy transferred to the surface is equivalent to heat, and leads to a spontaneous desorption of a small fraction of solute. If the collisions are infrequent, the displaced solute will simply resorb and conventional partitioning behavior will result. However, if the collisional frequency is high enough, the conventional equilibrium concentrations will not be restored. In other words, a balance will be struck between the frequency of collision and the rate of resorption.

Consider the equilibrium



where S, P, and SP are solute, particle, and reversibly-sorbed solute, respectively. It follows that

$$d[SP]/dt = k_1[S][P] - k_2[SP] \quad (1)$$

Equation 1 integrates to

$$[SP] = [SP_0] e^{-k't} + (k_1/k')[P][S_t](1-e^{-k't}) \quad (2)$$

where the number of adsorbable sites are considered to be in excess over solute, i.e.,  $[P] \approx [P_0]$ ,

$$[S_t] = [S] + [SP] \quad (3)$$

and

$$k' = k_1[P] + k_2 \quad (4)$$

At the moment of collision the particle receives an energy pulse that desorbs a small fraction of solute. If the fraction remaining on the particle is designated as  $\underline{f}$ , then multiplying the [SP] term in eq 2 by  $\underline{f}$  gives

$$[SP] = f\{[SP_0]e^{-k't} + (k_1/k')[P][S_t](1-e^{-k't})\} \quad (5)$$

Let  $\tau$  be the period between collisions. Just before the next collision, [SP] will be given by substituting [SP<sub>0</sub>] in eq 2 with the quantity in eq 5. Hence,

$$[SP] = (k_1/k')[P][S_t](1-e^{-k'\tau}) + fe^{-k'\tau}\{[SP_0]e^{-k'\tau} + (k_1/k')[P][S_t](1-e^{-k'\tau})\} \quad (6)$$

$$= (k_1/k')[P][S_t](1-e^{-k'\tau}) + fe^{-k'\tau}(k_1/k')[P][S_t](1-e^{-k'\tau}) + f[SP_0]e^{-2k'\tau} \quad (7)$$

Just before the subsequent collision,

$$[SP] = (k_1/k')[P][S_t](1-e^{-k'\tau}) + fe^{-k'\tau}(k_1/k')[P][S_t](1-e^{-k'\tau}) + f^2e^{-2k'\tau}(k_1/k')[P][S_t](1-e^{-k'\tau}) + f^2[SP_0]e^{-3k'\tau} \quad (8)$$

Equation (8) was obtained by multiplying eq 7 by  $\underline{f}$  and substituting the result into the [SP<sub>0</sub>] term in eq 2 as before. After  $\underline{n}$  collisions,

$$[SP] = (k_1/k') [P][S_t] (1-e^{-k'\tau}) \sum_{j=0}^n (fe^{-k'\tau})^j + f^n [SP_0] e^{-(n+1)k'\tau} \quad (9)$$

For large  $n$ , the summation  $\sum (fe^{-k'\tau})^n$  converges to  $1/(1-fe^{-k'\tau})$ , and the last term in eq 9 approaches zero. Hence,

$$[SP] = (k_1/k') [P][S_t] (1-e^{-k'\tau}) / (1-fe^{-k'\tau}) \quad (10)$$

The partition coefficient  $K$  can be written as

$$K = \frac{[SP]/[P]}{[S_t] - [SP]} \quad (11)$$

$$= \frac{k_1(1-e^{-k'\tau})}{k'(1-fe^{-k'\tau}) - k_1[P](1-e^{-k'\tau})} \quad (12)$$

The conventional distribution coefficient (i.e. without the collision effect)  $K_c$  is  $k_1/k_2$ . Equation 12 can be rearranged to

$$K = \frac{K_c(1-e^{-k'\tau})}{1 - fe^{-k'\tau} + K_c[P](1-f)e^{-k'\tau}} \quad (13)$$

Equation 13 is the general equation governing both particle-induced and conventional sorption. At low solids, the exponential term vanishes since  $\tau$  is large, and  $K=K_c$ . Thus, the difference in magnitude between conventional and collisional desorption is governed by  $\tau$ , the interval between collisions.

A potential difficulty with the above scheme is that Brownian collision of water molecules with the particle surface occurs much more often and with energies not much different than those

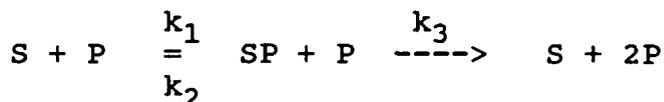
involved in interparticle collision. However, energy transfer in collisions between species of different size is much less efficient than those between similar sized particles. For example, the fraction of kinetic energy transferred ( $f_{\text{trans}}$ ) from one particle to the other in an elastic head-on collision is given by

$$f_{\text{trans}} = (4m_1/m_2)/(1+m_1/m_2)^2 \quad (14)$$

where  $m_1$  and  $m_2$  are the masses of the two particles involved, with particle 2 being considered to be initially at rest. For two particles of equal mass,  $f_{\text{trans}}=1$ , i.e. all the kinetic energy is transferred. Hence, the energy transferred during particle-particle collision is several orders of magnitude greater than that involved in water-particle collision.

### Discussion

DiToro's model for collisional desorption is based on the scheme



from which

$$K = \frac{K_C}{1 + [P]K_C k_3/k_1} \quad (15)$$

Lande (5) has objected to the scheme on the grounds that an equilibrium cannot include an irreversible step. Thus, the basis of eq 15 is uncertain, but it applies quite well to the experimental data at an empirical level. Equations 13 and 15 predict similar dependencies of  $K$  on particle concentration. Equation 13

can be rearranged to

$$K = \frac{K_c}{\frac{1 - fe^{-k'\tau}}{1 - e^{-k'\tau}} + \frac{K_c[P](1-f)e^{-k'\tau}}{1 - e^{-k'\tau}}} \quad (16)$$

At high [P],  $k_1[P] > k_2$  and  $k'\tau \approx k_1[P]\tau$  (from eq 4). Since  $\tau$  is inversely proportional to [P], the exponential term will be independent of [P]. Also, since  $f$  approaches 1, the term  $(1-fe^{-k'\tau})/(1-e^{-k'\tau})$  will be only slightly greater than 1, and equations 13 and 16 will be similar in form.

DiToro notes (1) that the coefficient ( $k_3/k_1$ ) in eq 15 tends to approximate one. The equivalent term in eq 16 is  $(1-f)e^{-k'\tau}/(1-e^{-k'\tau})$ . Equating this term to one gives

$$f = 2 - e^{k'\tau}$$

Mackay and Powers (4) calculated that the interval between collisions corresponding to a particle density of  $1.3 \times 10^{11}$  particles/L is approximately 1 hour. However, this value applies only to the initial collision, and  $\tau$  will be very much lower since multiple collisions occur before the particles fully separate.

Finally, given DiToro's success in applying eq 15 to a large body of sorption data (1), we recommend that the equation be retained with its constants redefined. If  $(1-fe^{-k'\tau})/(1-e^{-k'\tau})=1$  in eq 16, then eq 16 simplifies to

$$K = \frac{K_C}{1 + K_C[P]C_f} \quad (17)$$

where  $C_f$  is designated the collision factor and is defined as

$$C_f = (1-f)/(e^{k'\tau}-1)$$

$C_f$  is expected to be constant for a given solute/sorbent combination. Equation 17 is similar in form to eq 15, but has a defensible thermodynamic basis.

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