Sorption of Colloids, Organics, and Metals onto Gas-Water Interfaces

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Introduction

Colloids are found to favorably sorbed at gas-liquid interfaces (Fig. 1) under certain conditions in subsurface vadose zones and ocean surface. Thus, quantifying colloidal surface excesses is important for understanding and predicting partitioning, transport and transformations of colloids, and other organic and metal species complexed onto colloids in many natural environments. Although surface excesses of solutes can be determined by measuring changes in surface tension combining with the Gibbs adsorption equation (Eq.1), no methods for quantifying colloid surface excesses were available prior to this EMSP project. In this study we developed a bubble column method for measuring partition coefficients of colloids at air-water interfaces. The first measured partition coefficients of kaolinite and humic colloids at the air-water interfaces are reported. The bubble column method can also be used to identify surface exclusion of colloids at the air-water interface. This method permits quantification of surface activities of a wide range of inorganic, organic, and microbial colloids, as well as molecular species complexed onto colloids.

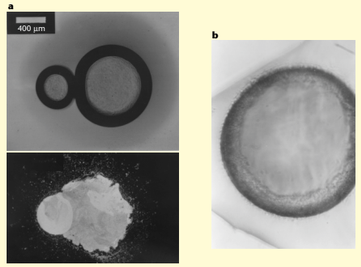


Fig. 1. Sorption of kaolinite clay (a) and bacteria (b) on the surfaces of air-bubbles.

The Gibbs adsorption equation

$$\Gamma = -\frac{C}{RT}\frac{d\gamma}{dC} \qquad (1)$$

is useful for molecular species by Measuring surface tension changes, *but not for colloids.*

Verification of the Bubble Column Method

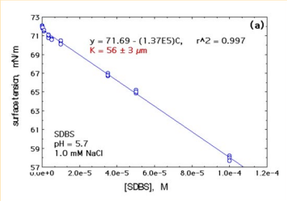
The bubble column method was tested by comparing the K value obtained from the bubble column method through Eq. (5), with the K value from surface tension measurements through Eq. (6), for dilute surfactant solutions of sodium dodecyl benzene sulfate (SDBS).

Rearranging Eq. (4) gives

$$K = \frac{AD}{afz}\ln\frac{C(z)}{C_b} \qquad (5)$$

Combining Eq. (1) and Eq. (3) gives

$$K = \frac{-1}{RT}\frac{d\gamma}{dC} \qquad (6)$$



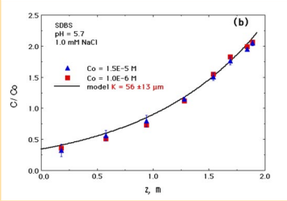


Fig. 3. Testing the bubble column method on SDBS solutions. (a) K = 56±3 µm, from surface tension measurements. (b) K = 56±13 µm, from the bubble column method. This agreement validated the bubble column method.

Examples of Partition Coefficients (K), Which Quantify Colloid Sorption at Air-Water Interfaces

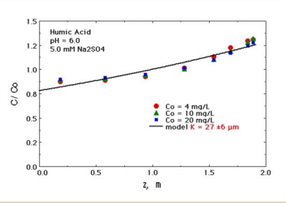


Fig. 4. Steady-state relative concentration profiles of humic acid in the bubble column. Data points are from column experiments conducted at the three indicated average humic acid concentrations. For the indicated solution chemistry, K = 27 ±6 µm.

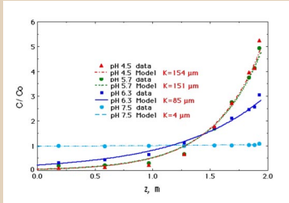


Fig. 5. Steady-state relative concentration profiles of Na-kaolinite clay particles in the bubble column. Data points are from column experiments conducted at the three indicated pH values. Note that kaolinite partitioning at air-water interfaces varies over a wide range, depending on pH.

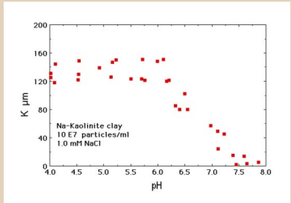


Fig. 6. The pH-dependence of K for Na-kaolinite.

Method

A bubble column device (Figure 2) was developed for quantifying colloidal surface excesses. Air is bubbled through the vertical column containing dilute aqueous suspension of the colloids. The rising bubbles sorb and carry the surface-active species upwards, then release them back to the solution at the free surface where the bubbles burst. The steady-state concentration profile reflects the balance between upward transport by partitioning onto rising bubbles and downward transport by eddy dispersion (Eq. 2),

$$af\Gamma = AD\frac{dC}{dz} \qquad (2)$$

where a is the average surface area per bubble, f is the bubble generation rate, Γ is the surface excess, A is the column cross-sectional area, D is the column eddy dispersion coefficient, C is the concentration in solution (suspension), and z is the vertical coordinate.

In dilute solutions, partitioning at the water-gas interface is given by

$$\Gamma = KC \qquad (3)$$

For surface-active molecules, K is the linear adsorption isotherm coefficient. In extending this approach to colloid systems, we define K as the colloid partition coefficient. It is expected that in many natural systems the suspended colloid concentration will be sufficiently dilute such that the linear K approximation is sufficient.

The steady-state ratio of the concentration at elevation z versus at the bottom of the column is an exponential profile.

$$\frac{C(z)}{C_b} = \exp\left(\frac{afKz}{AD}\right) \qquad (4)$$

By predetermining D, af, and measuring the steady-state concentration profile C[z], the partition coefficient K can be determined.

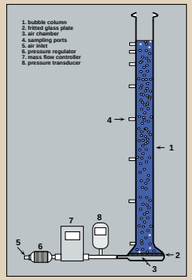
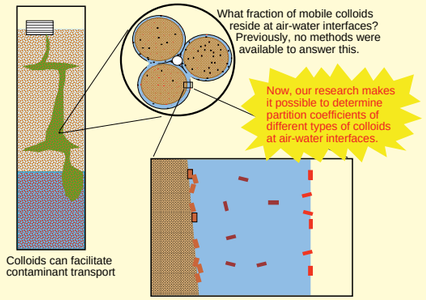


Fig. 2. Bubble Column Device

Vadose Zone Implications

The K values we measured for humic acid and kaolinite indicate that the amount of air-water interface-associated colloids is of the same order as that in suspension in partially-saturated soils (under similar solution chemistries). This result indicates that colloid partitioning at air-water interfaces of partially-saturated porous media can be much more significant than previously recognized.



Planned Activities

- Identify underlying mechanisms responsible for colloid sorption at air-water interfaces.
- Study partitioning at air-water interfaces in more complexed systems containing mixtures of heavy metals, natural organic matter, and organic contaminants.
- Test the feasibility of colloid release and mobilization for in-situ decontamination of sorbed metals and radionuclides.

Publication

Wan, J. and T. K. Tokunaga, Measuring partition coefficients of colloids at air-water interfaces, Environ. Sci. Technol., in press, 1998.

Conclusions

- We developed a bubble column method for quantifying colloid sorption at gas-liquid interfaces.
- The method was validated through comparing SDBS K values obtained through comparing conventional surface tension measurements with values obtained with the bubble column.
- The partition coefficients of clay and humic acid at air-water interfaces were obtained.
- This method will permit quantification of surface activities of a wide range of inorganic, organic, and microbial colloids, as well as molecular species complexed onto colloids.

Acknowledgment

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