MEASURING THE PARTITIONING OF SILVER TO ORGANIC CARBON USING
SOLUBILITY ENHANCEMENT

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Abstract—Ionic silver is toxic to aquatic organisms at low concentrations. However, complexation to binding sites on natural organic matter has been shown to reduce silver toxicity. Research indicates that there is a need to develop reliable methods for characterizing silver binding at very low silver ion concentrations where strong binding sites have a significant influence on silver speciation. Preliminary experimental results are provided that demonstrate strong silver binding in the presence of natural organic matter at very low silver ion concentrations.

Keywords—Silver Partitioning Organic carbon Solubility enhancement Toxicity

INTRODUCTION

Ionic silver can be toxic to aquatic organisms at very low concentrations. The U.S. Environmental Protection Agency criteria are 1.9 μg/L (18 nM) in salt water and 3.43 μg/L (34 nM) in freshwater [1] at a hardness of 100 mg/L CaCO₃. However, the bioavailability and, therefore, toxicity of silver in the water column and sediment are highly dependent upon the chemistry of the system [2–4]. In particular, silver complexation to natural organic matter (NOM) (more specifically dissolved organic carbon [DOC]) has been shown to reduce its bioavailability and toxicity [5–10]. The functional groups associated with NOM have been shown to vary in both their abundance and affinity for silver [11]. Research suggests that silver complexation to NOM at concentrations near the criteria levels (low nM) is influenced heavily by low-abundance, high-strength binding sites consisting of reduced sulfur species. At these low concentrations, it is difficult to measure directly the silver concentrations required to parameterize this complexation. Studies conducted at high silver concentrations tend to probe the more abundant, weaker sites, typically consisting of carboxylic, amino, and phenolic groups, resulting in an incomplete description of silver binding to NOM [11,12].

In order to study silver complexation to NOM at low silver concentrations, an experimental method is required that will maintain the silver ion concentration in the low ng/L to μg/L (10⁻¹² to 10⁻⁸ mol/L) range and allow for the quantification of both bound and ionic silver. A solubility-enhancement method using silver halide solids is presented below that fulfills both of these requirements.

Solubility enhancement procedure

The use of solubility enhancement to measure the complexation of organic chemicals to NOM has been used by a number of investigators [13–17]. However, the method appears not to have been used for measuring metal-NOM complexation.

Consider a system in which a silver halide solid is in equilibrium with an aqueous phase. The dissolution of the solid is described by a solubility product, $K_{sp}$. The solubility products for silver iodide and silver bromide are

$$K_{sp,AgI} = [Ag^+] [I^-]$$
$$K_{sp,AgBr} = [Ag^+] [Br^-]$$

The addition of halide to an equilibrated solution in contact with silver halide solid will cause the silver ion concentration to decrease as more silver halide precipitates to maintain solubility equilibrium (Eqn. 1a and b). The ranges of silver ion concentrations that can be achieved using these solids were calculated using the chemical equilibrium program MINEQL+ [18] (Fig. 1). The effect of the soluble silver iodide and silver bromide complexes are included in the calculation. The solubility products are listed in Table 1. By using the appropriate solid and halide concentrations, the silver ion concentration can be fixed between 1 pg Ag/L ($10^{-14}$ M) and 0.1 mg Ag/L ($10^{-8}$ M).

To quantify the partitioning of silver to NOM, silver halide solid, AgX(s), is encapsulated in a dialysis membrane container and placed in a solution of alkali halide at a concentration that will reduce the silver ion concentration to the desired concentration. The dialysis container keeps AgX(s) separate from the bulk solution while permitting the exchange of ions. Adding a known mass of particulate (=POC) and dissolved (=DOC) organic carbon to the solution results in the system depicted in Figure 2. Partitioning of silver to POC and DOC, as well as the formation of soluble silver-halide complexes (reactions B, C, and D), serve to dissolve silver from AgX(s). As this happens, the $[Ag^+] [X^-]$ equilibrium readjusts. If the amount of halide ion liberated from the solid is comparable to the initial concentration in the bulk solution, the equilibrium between silver and halide will shift, producing a lower silver ion concentration than was present initially.

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A sample of the bulk solution is filtered and the filtrate is analyzed to determine the total dissolved silver and halide ion concentration. The silver ion concentration is obtained from the halide ion concentration and the equilibrium expression (Eqn. 1). The amount of silver sorbed to DOC, $\Gamma_{DOC}$, moles of sorbed silver/kg organic carbon, can be calculated using mass action and mass balance. The dashed line represents the output generated using the experimentally determined $K_p$ for AgI(s) (Table 1).

\[ K_p^{AgI} = \frac{\Gamma_{DOC}}{[Ag^+]^2} \]

The apparent partition coefficients for DOC and POC ($K_{PDOC}^{app}$ and $K_{POC}^{app}$, [L/kg organic carbon], respectively) are calculated from the relationship

\[ K_p^{app} = \frac{\Gamma}{[Ag^+]} \]

In the absence of direct halide ion measurements, partitioning of silver to POC and DOC can be determined by modeling the solution-solid system using a chemical equilibrium program such as MINEQL+. Partitioning to both forms of organic carbon is modeled as a complexation reaction. The silver source is the dissolution of the silver halide solid. Partitioning is quantified by adjusting the formation constants of the POC and DOC complexation reactions to reproduce the experimental silver measurements. This procedure is discussed below.

Table 1. Comparison of solubility products

<table>
<thead>
<tr>
<th>Solid</th>
<th>Literature log ($K_w$)</th>
<th>Experimental log ($K_w$)</th>
<th>No. of samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgI(s)</td>
<td>-16.070</td>
<td>-17.3 (-18.5,-17.1)*</td>
<td>6</td>
</tr>
<tr>
<td>AgBr(s)</td>
<td>-12.270</td>
<td>-12.3 (-12.7,-12.0)*</td>
<td>4</td>
</tr>
</tbody>
</table>

* $K_w$ values from MINEQL+ [18] database.

The average experimental values are quoted; the minimum and maximum experimental values are placed in parentheses.

For this method to work, complexation to POC and/or DOC must be strong enough that the resulting silver concentration on the particles or in the dissolved phase is large enough to measure.

**MATERIALS AND METHODS**

**Verification of solubility products**

Experiments were performed to evaluate the applicability of the solubility-enhancement procedure and to verify the solubility products ($K_w$) of the two silver halides. The solubility product of solid silver bromide, AgBr(s), was measured directly; no solubility enhancement was used. A dialysis container was prepared using dialysis membrane tubing with a molecular weight cutoff of 12,000 to 14,000 Daltons (Carolina Biological Supply, Burlington, NC, USA). Approximately 0.2 g of Acros 99% silver bromide (Chemical Abstracts Service [CAS]: 7785-23-1; Acros Organics, Morris Plains, NJ, USA) were added to a 15-cm section of tubing, which was tied off with 4-lb test monofilament line and placed in 18-MΩ cm deionized water in the dark with constant stirring. The bulk solution was sampled after 26 and 29 d and the samples were analyzed for total silver by flame atomic absorbance spectrometry. This experimental procedure was performed in duplicate.

Solid silver iodide, AgI(s), is several orders of magnitude less soluble than silver bromide. A solubility-enhancement procedure was used in which thiosulfate, a ligand with a known silver formation constant, was added to the bulk solution to ensure that the total silver in solution would be high enough to measure with flame atomic absorbance spectrometry. A dialysis container with approximately 0.01 g of Acros 99% silver iodide (CAS: 7783-96-2) was placed in a 10⁻³-M sodium thiosulfate solution prepared with Fisher Scientific certified sodium iodide (CAS: 6861-82-5; Fisher Scientific, Fair Lawn, NJ, USA) in the dark with constant stirring. Sodium thiosulfate, Na₂S₂O₃ (Fisher Scientific certified CAS: 7772-98-7), was added from a stock solution to achieve 10⁻²-M thiosulfate in the bulk solution. The bulk solution was sampled after 6, 7, 9, and 10 d of stirring. All samples were analyzed for total silver by flame atomic absorbance spectrometry. A second experiment was performed with AgI(s) using the same procedure described above except the initial iodide and thiosulfate concentrations in the bulk solution were 0 and 2 x 10⁻³ M, re-
approximately 21% of the AHA material is retained on a 0.45-
The AHA solutions primarily were colloidal. At pH 7, average, 11.4% (on a mass basis) of the bulk material dissolved.

Silver partitioning
Silver partitioning experiments were performed using two sources of organic carbon: Pahokee peat ([PP]; International Humic Substances Society, Denver, CO, USA) and Aldrich humic acid ([AHA]; CAS: 68131-04-4). Experiments were conducted to determine the fraction of PP that dissolved in deionized water. A known mass of peat was placed in deionized water, stirred, and filtered using a 1.2-μm glass fiber filter. On average, 11.4% (on a mass basis) of the bulk material dissolved, from which the concentration of POC and DOC in solution can be determined. It is assumed that the particulate and dissolved fractions in solution each have the same organic carbon content as the bulk material: 45.7% organic carbon by mass. Aldrich humic acid is 38.6% organic carbon by mass. The AHA solutions primarily were colloidal. At pH 7, approximately 21% of the AHA material is retained on a 0.45-

\[
\text{Set}^a | \text{POC}^b (\text{kg-org C/L}) | \text{DOC}^b (\text{kg-org C/L}) | \text{Initial halide} | \text{pH Range} | p[Ag^{0}]_{\text{POC}} | p[Ag^{0}]_{\text{DOC}} | p[Ag^{+}] | \log (K_{\text{PP}}^{\text{pp}})_{\text{POC}} | \log (K_{\text{PP}}^{\text{pp}})_{\text{DOC}}
\]

| AgI-PP-1 | 8.10 \times 10^{-4} & 1.05 \times 10^{-4} & 8.35 \times 10^{-7} & 5.76-5.82 & 5.0 & - & 12.1 & 10.2 & -
| AgI-PP-2 | 8.16 \times 10^{-4} & 1.05 \times 10^{-4} & 1.00 \times 10^{-3} & 5.70-6.05 & 6.6 & - & 12.4 & 8.8 & -
| AgBr-PP-1 | 8.11 \times 10^{-4} & 1.05 \times 10^{-4} & 1.75 \times 10^{-5} & 5.80-5.95 & 7.4 & - & 12.6 & 8.0 & -
| AgBr-PP-2 | 8.12 \times 10^{-4} & 1.05 \times 10^{-4} & 2.50 \times 10^{-5} & 5.90-5.95 & 7.1 & - & 12.7 & 8.6 & -
| AgBr-AHA-1 | 8.11 \times 10^{-4} & 1.05 \times 10^{-4} & 2.34 \times 10^{-4} & 5.70-6.05 & 5.8 & 6.1 & 6.7 & 6.0 & 6.6
| AgBr-AHA-2 | 8.10 \times 10^{-4} & 1.05 \times 10^{-4} & 8.00 \times 10^{-3} & 5.70-6.05 & 7.6 & 7.3 & 10.2 & 5.7 & 6.8

\[K_{\text{PP}}^{\text{pp}}\] values have been adjusted to correspond to pH = 5.9 using log \( (K_{\text{PP}}^{\text{pp}})_{\text{POC}} = \log (K_{\text{PP}}^{\text{pp}})_{\text{DOC}} + \Delta pH. \]

As AgI-PP-1 and AgI-PP-2. One notable difference is that, in addition to measuring the sorbed silver from the filter residue for each sample, the filtrate passing through the 0.45-μm filter was analyzed for total silver. The AgBr-AHA-1 experiment was performed in similar fashion but without filtration. The entire sample was analyzed for total silver. The AgBr-AHA-1 experiment, like the AgBr-PP-1 experiment, included controls with no silver halide in the dialysis container. Any silver measured in samples from the controls was subtracted from the corresponding samples from systems with silver halide solid in the dialysis container.

Data analysis
Total soluble silver was determined from the sample filtrates, or, in the case of the Aldrich humic acid, from the entire sample. Total soluble silver is the sum of \([AgX\text{ complexes}], [Ag^+]\), and \([Ag = DOC]\). The silver sorbed to POC, \(\Gamma_{\text{POC}} \) (moles Ag/kg organic carbon), can be expressed as a concentration \([Ag = POC]\)

\[\text{POC} \rightarrow \Gamma_{\text{POC}} \] (3)

where \(\text{POC} \) is the total POC concentration. Partitioning to both POC and DOC are modeled as complexation reactions

\[\text{Ag}^+ \leftrightarrow \text{Ag} = \text{POC} \] (4a)
\[\text{Ag}^+ \leftrightarrow \text{Ag} = \text{DOC} \] (4b)

The equilibrium equations for these reactions are

\[K_{\text{POC}} = \frac{[\text{Ag} = \text{POC}]}{[\text{Ag}^+]} \] (5a)
\[K_{\text{DOC}} = \frac{[\text{Ag} = \text{DOC}]}{[\text{Ag}^+]} \] (5b)

These equilibrium constants can be related to an apparent partition coefficient, \(K_{\text{PP}}^{\text{pp}}\)

\[K_{\text{PP}}^{\text{pp}} = \frac{\Gamma_{\text{POC}}}{[\text{Ag}^+] \text{POC}_T[\text{Ag}^+] = K_{\text{POC}} \text{POC}_T} \] (6)

A similar equation can be written for DOC.

The solution of the chemical equilibrium equations is simplified by using MINEQL+, which implements the equations in the appendix. Mass balance equations for the total component concentrations are

\[\text{AgBr-AHA-1} \rightarrow \frac{\Gamma_{\text{POC}}}{[\text{Ag}^+] \text{POC}_T[\text{Ag}^+] = K_{\text{POC}} \text{POC}_T} \]
\[ \text{Ag}_t = [\text{Ag}^+] + [\text{AgX complexes}] + [\text{Ag} = \text{DOC}] \\
+ [\text{Ag} = \text{POC}] \\
\]
\[ X_t = [X^-] + [\text{AgX complexes}] \]

Silver halide solid, AgX(s), is entered as a fixed solid (corresponding to an infinite reservoir), and its dissolution serves as the source of silver to the system. Forcing the presence of AgX(s) eliminates the need to supply an input value for \( \text{Ag}_t \); it is left as 0. The value of \( \text{Ag}_t \) at equilibrium is calculated in MINEQL+ based on the silver ion concentration, which is constrained according to the solubility of AgX(s)

\[ K_{\text{sp,AgX}} = [\text{Ag}^+][X] \]

Initially, the concentration of \( X_t \) is entered as the nominal value added to the solution. However, this value is updated during the MINEQL+ calculation to reflect increases in halide concentration caused by the dissolution of AgX(s).

The unknowns in the problem are the formation constants for the Ag = POC and Ag = DOC species. These unknowns are estimated using trial and error by varying their values until the computed dissolved [AgX complexes] + [Ag⁺] + [Ag = DOC] and particulate [Ag = POC] silver concentrations match the observations. It should be noted that this procedure is a general one and is changed to suit the needs of the particular experimental set.

The values of the apparent partition coefficient values for POC and DOC are calculated by dividing \( K_{\text{f,POC}} \) and \( K_{\text{f,DOC}} \) (obtained in MINEQL+) by \( P_{\text{OC}_t} \) and \( P_{\text{DOC}_t} \) respectively. The values of POC and DOC are based on the mass of DOC added.

**RESULTS AND DISCUSSION**

The measured silver halide solubility product constants are listed in Table 1. For AgBr(s), there is very good agreement between the tabulated (MINEQL+) and the experimentally determined value of the log \( K_{\text{sp}} \). However, there is a discrepancy between the two \( K_{\text{sp}} \) values of AgI(s). The silver iodide solid appears to be significantly less soluble than predicted by MINEQL+ (Fig. 1). Previous determinations indicate that a log \( K_{\text{sp}} \) of \(-17.3 \) is possible [20]. The experimentally determined \( K_{\text{sp}} \) for AgI(s) and AgBr(s) are used in analysis of the partitioning experiment data.

The solubility-enhancement procedure is able to generate apparent partition coefficient data over a wide range of silver ion concentrations (Table 2 and Fig. 3). The experiments conducted at the lower silver ion concentrations, those employing AgI(s) as the silver source (AgI-PP-1 and AgI-PP-2), have the highest partition coefficients. Because the silver was not measured in the filtrate from the samples in these two experiment sets, only results for silver adsorption to POC were obtained. Sensitivity analyses were performed in MINEQL+ to assess the potential errors associated with ignoring the sorption of silver to DOC when analyzing the experimental results. These analyses demonstrate that, for the AgI-PP-1 set, the potential error in the computed \([\text{Ag}^+]\) value at most is a factor of approximately 1.5 for \( K_{\text{sp,AgBr}} \) equal to 0.1 to 10 times the value of \( K_{\text{sp,AgI}} \). The AgI-PP-2 set, which had a higher initial total iodide concentration (\( \sim 10^{-5} \) M as compared to \( \sim 10^{-6} \) M), shows almost no sensitivity to similar variations in the value of \( K_{\text{sp,AgBr}} \); the maximum potential error in \([\text{Ag}^+]\) is approximately 5%. It appears that, as long as the bulk total halide concentration is high enough, sorption of silver to POC can be quantified independently of sorption to DOC.

The results for the AgBr-PP-1 include an estimate for both \( K_{\text{sp,AgBr}} \) and \( K_{\text{sp,AgI}} \). It is interesting to note that \( K_{\text{sp,AgI}} \) is greater than \( K_{\text{sp,AgBr}} \). We have no explanation for this result. The AgBr-PP-2 set was modeled in MINEQL+ as a DOC-only system because the samples taken from the colloidal solution were not filtered before analysis. At the higher silver concentrations of this experiment, \( K_{\text{sp,AgBr}} \) is considerably lower, as expected.

**Silver–organic carbon partitioning model**

The data demonstrate that the partition coefficient decreases with increasing silver ion concentration. To provide a mechanistic representation of silver binding, the data are fit with a Langmuir isotherm. Not enough data were available to model DOC (\( K_{\text{f,DOC}} \)) and POC (\( K_{\text{f,POC}} \)) sorption separately. Therefore, the regression is performed using all partitioning data and it is assumed that \( K_{\text{f,POC}} = K_{\text{f,DOC}} \) [21]. Previous research suggests that silver partitioning to NOM involves several different site types [11,12]. Therefore, a Langmuir multisite model of the following form is used:

\[ K_{\text{p,app}} = \frac{\Gamma}{[\text{Ag}^+]} = \sum_{i=1}^{n} \frac{\Gamma_{\text{max},i}}{K_{\text{p,app},i}} + [\text{Ag}^+] \]

The fitting parameters are \( \Gamma_{\text{max},i} \), the site density of the \( i \)th site, and \( K_{\text{p,app},i} \), the intrinsic partition coefficient of the \( i \)th site. The data were fit separately using a one- and two-site model (Table 3). Both models produced reasonable fits to the data. The two-site model yields a high-energy site and a low-energy site. However, the resulting fit to the experimental data are almost indistinguishable from the one-site model (Fig. 3, solid line).
This differs from the result of two (or more) discrete binding sites that can produce a curve with a number of shoulders corresponding to the onset of binding to the successive site types. It is possible the lack of evidence for multiple binding sites is caused by the limited amount of experimental data taken. The rest of the discussion will focus on the results of the one-site model.

The parameters associated with the one-site model are compared to the results from studies by Smith et al. [12] and Adams and Kramer [22] of silver complexation to particulate and colloidal forms of samples from the receiving waters of a wastewater treatment plant (Table 4). Stability constants (log $K_{AgL}$) and the associated total sulfur ($-II$) ligand concentrations ($L_{-II}^{Ag}$) [12,22] calculated from silver titrations are used together with estimates of the POC and DOC concentrations in the sample area [12,23,24] to determine the values of $K_{w}$ and $\Gamma_{\text{max}}$. The intrinsic partition coefficient, $K_{w}$, obtained from the solubility-enhancement procedure compares very favorably with the estimates from these studies. This suggests the strong binding of silver observed at low concentrations (Fig. 3) is due to the presence of reduced sulfur groups in the organic carbon source used. The site density value obtained in this study is somewhat lower than the estimates from the other studies. It is possible that the organic matter in these other studies possessed a higher density of reduced sulfur sites, especially since the samples were collected downstream of a wastewater treatment plant.

CONCLUSION

This study provides an analytical method for investigating and characterizing silver binding to NOM, in the form of POC and DOC, over a range of low silver ion concentrations that span environmentally realistic concentrations. Preliminary investigations suggest the presence of strong silver binding at very low silver ion concentrations. However, additional data are required to provide a more thorough characterization of this binding behavior for use in predictive toxicity models.

### Acknowledgement

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### REFERENCES

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**APPENDIX**

MINEQL+ [18] aqueous species tableaux for the AgBr(s) and AgI(s) system. In MINEQL+, species that also are components (H₂O, H⁺, Ag⁺, and Br⁻ or I⁻) are not included in the species list in the tableau (left-most column).

<table>
<thead>
<tr>
<th></th>
<th>H₂O</th>
<th>H⁺</th>
<th>Ag⁺</th>
<th>X⁻</th>
<th>Log Kᵢᵃ</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH⁻</td>
<td>1</td>
<td>−1</td>
<td></td>
<td></td>
<td>−13.998</td>
</tr>
<tr>
<td>AgPOC</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td>log Kᵢ POC</td>
</tr>
<tr>
<td>AgDOC</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td>log Kᵢ DOC</td>
</tr>
<tr>
<td>AgOH</td>
<td>1</td>
<td>−1</td>
<td>1</td>
<td></td>
<td>−12.000</td>
</tr>
<tr>
<td>Ag(OH)₂</td>
<td>2</td>
<td>−2</td>
<td>1</td>
<td></td>
<td>−24.000</td>
</tr>
</tbody>
</table>

\[ X = \text{Br}^- \quad X = \text{I}^- \]

\[ \text{AgX} = 1 \quad 1 \quad 4.2400 \quad 6.6000 \]
\[ \text{AgX}_2 = 1 \quad 2 \quad 7.2800 \quad 10.680 \]
\[ \text{AgX}_3 = 1 \quad 3 \quad 8.7100 \quad 13.370 \]
\[ \text{AgX}_4 = 1 \quad 4 \quad 8.100 \quad 14.080 \]

\[ \text{H}^+ \quad \text{Ag}^+ \quad X^- \]

*Kᵢ refers to the equilibrium constant for the formation reaction. The given values are those from the MINEQL+ database.