

# Distribution of Counterions at the Solid-Water Interface

J. F. McCarthy,<sup>1</sup> P. R. Jemian,<sup>2</sup> L. Liang<sup>1</sup>

<sup>1</sup> Oak Ridge National Laboratory, Oak Ridge, TN, U.S.A.

<sup>2</sup> University of Illinois/UNICAT

## Introduction

The goal of this research was to determine the feasibility of using anomalous ultra-small-angle x-ray scattering (AUSAXS) to determine the ionic distribution at a solid-water interface by measuring the counterion concentration around an aquatic colloidal particle.

Information on the counterion distribution at the surface-water interface of colloidal particles is essential for quantitative determination of interaction forces arising from two overlapping electric double layers when particles encounter one another. This information is generally estimated indirectly. We sought to evaluate whether the dimensions of the condensed counterion layer could be directly measured by using AUSAXS. To the best of our knowledge these measurements have never been attempted in a system of charged mineral particles in an aqueous solution.

## Materials and Methods

The specific objective of the initial study was to detect and measure the thickness of a condensed layer of electron-dense  $\text{Tl}^{+1}$  counterions around a silica colloid using AUSAXS approaches. We chose silica because the low  $\text{pH}_{\text{zpc}}$  of the material, allowing a negative charges on the particles throughout the experimental pH of  $\sim 4$  to 7. Cationic  $\text{Tl}^{+1}$  was used as the counterion because of its L(III) absorption edge. Anomalous scattering techniques were used to identify the contribution of the hollow shell of  $\text{Tl}^{+1}$  counterions to the total scattering intensity of the silica-Tl system. We wished to obtain scattering attributable to the silica colloid by itself, and to the “hollow shell” of  $\text{Tl}^{+1}$  counterions in the condensed layer surrounding the colloids. Parallel control solutions containing  $\text{Na}^{+1}$  instead of  $\text{Tl}^{+1}$  were included to determine the dimensions of the silica colloids in the absence of an x-ray scattering shell of counterion.

## Results

A silica concentration of 0.5% (w/v) provided an adequate signal while minimizing aggregation. The scattering curves for the colloids in a Na-counterion system are shown in Fig. 1 (upper panel). The data were fit using a polydisperse core-shell model. To evaluate the dimensions of the core, the scattering curves in the Na system were analyzed with the model parameters adjusted so that the shell thickness was fixed at a very small value ( $0.005 \text{ \AA}$ ), and the electron density of the shell was set to that of the aqueous solvent. The estimated radius of the particle core ( $98 \text{ \AA}$ ) is similar to the  $100 \text{ \AA}$  nominal radius provided by the manufacturer and to the particle size measured by photon correlation spectroscopy. The fitted values of the electron density of the  $\text{SiO}_2$  core and the aqueous solvent ( $5.9\text{e-}5$  and  $1.02\text{e-}5 \text{ \AA}^{-2}$ , respectively) were very close to the theoretical values ( $5.6\text{e-}5$  and  $9.4\text{e-}6 \text{ \AA}^{-2}$ , respectively).

The scattering data for the colloids in a Tl system (Fig. 1, lower panel) were fitted using the same model, with the core dimension and the electron density of the core and solvent fixed at the values indicated above. The fitted shell thickness was very small ( $0.06 \text{ \AA}$ ), and the electron density of the shell was approxi-

Fit Thickness of Thallium Counterion Shell

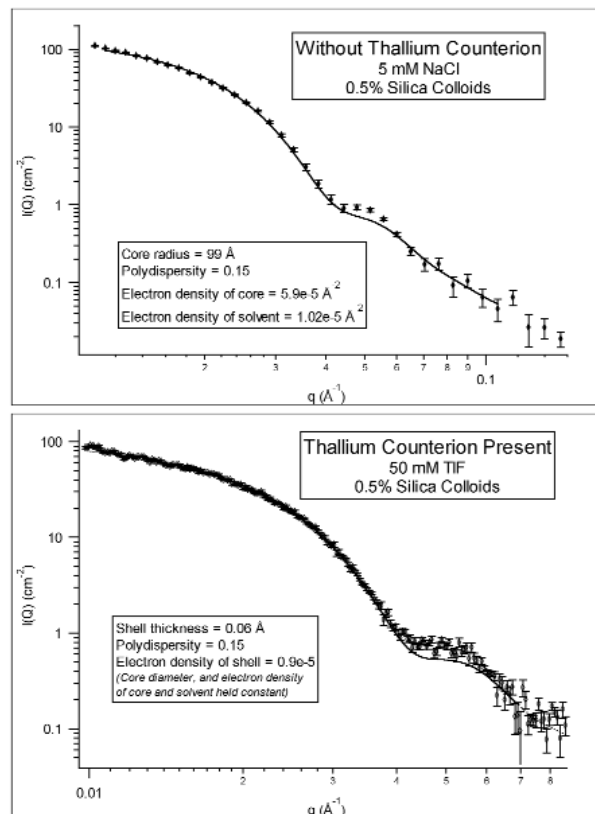


FIG. 1.

mately the same as that of the solvent. We concluded that the dimension of the  $\text{SiO}_2$  core surrounded by the electron-dense Tl counterion shell could not be distinguished from that of the core in a system of Na-counterions that contribute negligibly to scattering.

We evaluated whether anomalous scattering measurements improved differentiation of subtle signals from the Tl counterions. We measured scattering at four energies, shown in Table I. The anomalous dispersion terms for thallium (electron density = 81 electron units [eu] can be calculated<sup>1</sup> as  $f = Z + f' + i f''$  (Table I). The value  $f'$  is the effective number of electron decrease experienced at the different energies. Thus, the effective electron density of Tl was varied from 69 eu to 62 eu.

Table I. Effective Electron Densities of Thallium

Energy (eV) used in AUSAXS Experiment	$f'$	Effective Electron Density (eu)
12485	-11.49344	69.5
12585	-13.17679	67.8
12625	-14.74516	66.3
12654	-19.35	61.6

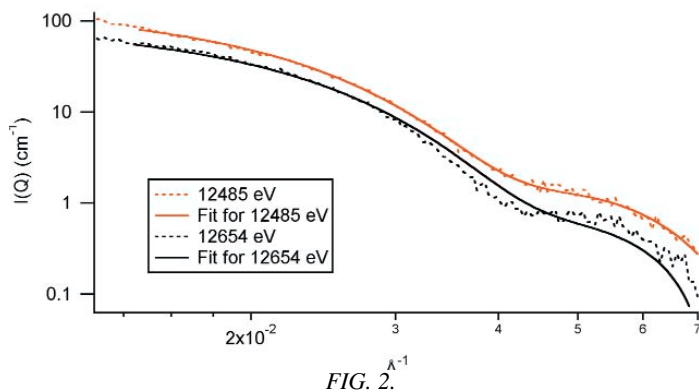


FIG. 2.

Scattering curves for the two extreme energies (12485 and 12654 eV) are shown in Fig. 2. First, the data at 12485 eV, representing the maximum thallium electron density used in the experiment, were fit using the polydisperse core-shell model. The initial parameter estimates were not constrained by those obtained previously using the Na-based colloid system, shown in the upper panel of Fig. 1. The estimated parameter values were:

Core radius = 70.7 Å

Shell thickness = 1.1 Å

Polydispersity = 0.23

Electron density of the Tl shell =  $9.8e^{-4} \text{ \AA}^{-2}$

This electron density corresponds to an aqueous concentration of Tl in the counterion shell of 68 M, which is more than 50-fold higher than that predicted from theoretical calculations of the coion and counterion distribution around a charged silica surface under the conditions of this experiment.

The data at 12654 eV were then evaluated by fixing the core

radius, shell thickness, and polydispersity to the values above, and fitting the electron density of the shell. The estimated electron density of the shell would be reduced from  $9.8e^{-4} \text{ \AA}^{-2}$  (above) to  $9.14e^{-4} \text{ \AA}^{-2}$  if the difference between the scattering curves reflected only a systematic variation in the effective electron density at the two energies. The latter value is the calculated electron density of a 68 M solution of Tl when the effective electron density of the Tl is reduced to 62 eu at 12654 eV. However, the fitted electron density of the Tl counterion shell is  $7.0e^{-5} \text{ \AA}^{-2}$ , which corresponds to an effective electron density of only 43 eu, far below the lowest possible effective electron density for a thallium atom.

The differences between the scattering curves in Fig. 2 cannot be attributed to differences in the effective electron densities at the two energies. The results may be complicated by the tendency of the colloids to undergo some degree of aggregation over time. The scattering curves shown above did not form a linear Guinier region over a wide range of low  $Q$ . The results were consistent with formation of dimers, trimers, and larger aggregates, and the abundance of these small aggregates appeared to increase over time. A series of five samples were measured consecutively at each energy. Thus, the data from the different energies represent a time sequence with delays of several hours between measurements at each energy for any individual sample. Although the bulk samples appeared to be colloidally stable, formation of small aggregates lead to increasing polydispersity, which may have obscured any differences that might have been evident due to scattering from the counterion shell.

## Reference

Cromer and Liberman, *J. Chem. Phys.* **53**:5 (1970).