

# Structure of a Crystal Growth Inhibitor Adsorbed at the Barite (001)-Water Interface

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## Introduction

The barite-water interface has been well-studied because of the problem of barite scale formation in the petroleum industry [1]. Barite precipitates when sulfate-rich seawater reacts with barite-rich sedimentary formation waters, forming scale deposits that restrict flow in pipes used for petroleum production. Most relevant studies to date have concentrated on understanding the mechanisms of barite crystal growth in the presence and absence of growth inhibitors because barite scale formation can be impeded by the addition of growth inhibitors [2]. A widely studied organic growth inhibitor is 1-hydroxy ethane-1, 1-diphosphonic acid (HEDP), known to effectively inhibit the growth of barite scales. We report on the use of x-ray reflectivity (XRR) to probe the structure of HEDP adsorbed to barite-water interface surfaces to gain insight into the mechanism of growth inhibition [3].

## Methods and Materials

Single crystals of optically clear, natural barite were cleaved to expose (001) surfaces. Cleavage of barite in air was followed quickly (< 1 min) by immersion of the cleavage surface in deionized water at room temperature and by mounting of the crystal in the XRR cell.

Experiments were performed in a static thin-film configuration with a water layer between the barite surface and an 8- $\mu\text{m}$  Kapton film. HEDP adsorption was performed on numerous samples both in the sample cell and before introduction to the XRR cell. The samples were exposed to concentrations and pHs ranging from 20  $\mu\text{M}$  at a pH of 6.4 to 100 mM HEDP solution at a pH of 8.9. Previous powder adsorption isotherm studies of HEDP on barite indicate that HEDP adsorption saturates above a solution concentration of  $\sim 20 \mu\text{M}$ , with some sensitivity to pH.

Synchrotron XRR measurements were made at the APS (beamlines 1-BM, 12-ID, 11-ID, and 12-BM) by using monochromatic x-rays ( $\Delta E/E = 10^{-4}$ ). Photon energies ranging from 15 to 16.3 keV were used for different

experiments. The background-subtracted reflectivity was measured with a rocking scan for all points. The reflectivity was monitored at selected scattering conditions to look for any x-ray-induced changes to the interfacial structure. No significant x-ray-induced damage was observed.

## Results

The reflectivity of the barite(001)-water interface is plotted for both a freshly cleaved surface in contact with deionized water and a surface after exposure to a 100-mM solution of HEDP at a pH of 8.9 (Fig. 1). The data show significant changes in the reflectivity between the Bragg peaks, indicating that there was significant adsorption of HEDP to the terrace areas under these conditions. While the reflectivity decreases substantially (by factors of  $\sim 100$ ) between the Bragg peaks, the reflectivity near  $Q = 2.5 \text{ \AA}^{-1}$  changes only slightly. This implies that

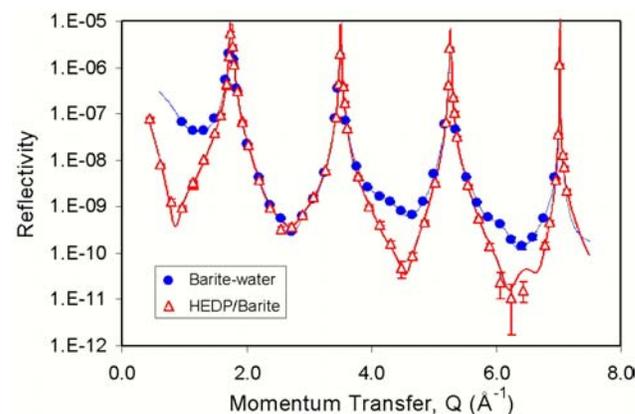


FIG. 1. High-resolution XRR data of the barite(001) water interface in contact with deionized water [4] and after exposure to a 100-mM solution of HEDP at a pH of 8.9. The solid lines correspond to the best-fit structures for the clean and HEDP-exposed surfaces and provide a quantitative agreement with the experimental data.

these changes are not primarily associated with any roughening of the surface but are instead caused by the orientation and density of HEDP molecules.

The structure of the barite-water interface in the absence of HEDP was described previously [4] and included both the expected structural relaxations near the barite-water interface and the adsorption of water to the barite surface to compensate for the Ba-O bonds broken during cleavage. No additional structuring of the water near the interface was observed.

The structure of adsorbed HEDP molecules was determined by comparing these high-resolution reflectivity data to atomistic structure factor calculations of HEDP-barite interfaces, as described for the barite-water interface [4], and by allowing a rigid HEDP molecule to translate and rotate above the barite surface. A calculation of the best-fit model of HEDP adsorption, shown in Fig. 1, provides quantitative agreement with the XRR data. This model includes a dense layer of HEDP molecules having a density of  $0.9 \pm 0.2$  per barite surface unit mesh. The HEDP molecule is oriented parallel to the barite surface.

## Discussion

We observed the structure of HEDP adsorbed at the barite(001) surface at a solution concentration of 100 mM. Through a separate series of measurements as a function of HEDP concentration (not shown), we find that HEDP adsorbs to the barite surface in significant quantities only when solution concentrations exceed 1 mM. This observation contrasts strongly with previous powder dissolution studies showing that adsorption of

HEDP reached saturation coverage at concentrations of  $\sim 20 \mu\text{M}$  and that this adsorption plateau is correlated with inhibition of barite crystal growth. This suggests that the inhibition of barite growth is primarily due to the adsorption of HEDP at steps. Step-specific adsorption is not visible to the XRR because of the low step densities of the cleavage surfaces used in the XRR studies.

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## References

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