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ANOMALOUS SMALL ANGLE X-RAY SCATTERING STUDIES OF HEAVY METAL ION SOLVATION BEHAVIOR IN CLAY MINERALS

Kathleen A. Carrado*, P. Thiyagarajan†, Randall E. Winans, and Kang Song
Chemistry Division and †Intense Pulsed Neutron Source Division
Argonne National Laboratory, 9700 S. Cass Ave., Argonne, IL 60439

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*author to whom all correspondence should be addressed.

ANOMALOUS SMALL ANGLE X-RAY SCATTERING STUDIES OF HEAVY METAL ION SOLVATION BEHAVIOR IN CLAY MINERALS

Kathleen A. Carrado*, P. Thiyagarajan†, Randall E. Winans, and Kang Song
Chemistry Division and †Intense Pulsed Neutron Source Division
Argonne National Laboratory, 9700 S. Cass Ave.; Argonne, IL 60439

ABSTRACT

We have exploited anomalous small angle x-ray scattering (ASAXS) to monitor the solvation behavior of Cu(II), Er(III) and Yb(III) ions within the interlayers of the natural aluminosilicate clay mineral montmorillonite. The ASAXS technique can reveal the distribution of specific metallic species within a heterogeneous and disordered matrix. The variations of signal intensity as a function of absorption energy were monitored for all of the metal-clays as a function of hydration. Two different hydration levels were probed: as prepared at ambient conditions, or so-called "dry" powders, and "wet" pastes. ASAXS intensities should increase with absorption energy if the metal ion is associated with the interlayer solvent (water in this case), and decrease if the metal ion is associated with the solid matrix. The results show that: (1) Cu(II) is solvated within the interlayers of the wet sample, as expected, and (2) Er(III) and Yb(III) decrease in ASAXS intensity with increased hydration. This latter result was not expected and there is speculation that these ions have associated as hydrolyzed products with the clay surface. The basic principles underlying SAXS and ASAXS will also be presented in this paper.

INTRODUCTION

Clay Minerals

Our interest in clays in terms of fuels science applications has two origins: (1) they are an inherent constituent in the mineral matter of coal and (2) their use as catalysts or catalyst supports in such processes as heavy petroleum upgrading. Small amounts of metal loadings on clays has relevance to both of these facets. Smectite clay minerals are layered metal silicates whose sheets can swell to incorporate up to several layers of water molecules. Each sheet is made up of one octahedral metal oxide layer, usually aluminum or magnesium, that is sandwiched by two tetrahedral silicate layers. Isomorphous substitutions within this framework give rise to a net negative charge on the lattice that is compensated for by the presence of exchangeable ions within the hydrated interlayer. Clays have a long history of applications as catalysts, catalyst supports, adsorbents, and ion-exchangers[1]. They are also prevalent in the mineral matter of coal, effecting it's combustion, processing, and conversion properties[2].

Clay minerals can incorporate heavy metal ions both within the lattice framework and between the interlayer regions. Our ASAXS investigation into the former situation has been published elsewhere[3]. For the latter case, clays ion-exchanged with various transition metal and lanthanide ions (Fig. 1), have been examined in hydrated and non-hydrated forms. The exchangeable interlayer metal ions impart a surface acidity on the clay that is variable depending upon the type of metal cation and the amount of water present within the interlayer[1]. This surface acidity is vital to many hydroprocessing reactions of importance to petroleum refining, for example. In addition to catalytic applications, these experiments are also pertinent to the structure, diffusion, and reactivity of species involved in, for example, environmental remediation issues. A preliminary report of Er(III)-clay ASAXS[3] has now been expanded to include several different metal ions.

SAXS And ASAXS Methodology

A description of both local and long-range atomic order associated with molecular assemblies in disordered media is essential for understanding the molecular basis for such issues as catalysis. Examples of such order include the structure and dynamics of molecular catalysts in solution, and the distribution of solvent, solute, and counterions around catalytic surface sites. X-ray scattering provides a powerful tool for the measurement of long-range atomic order in globally disordered media. Disordered systems far more frequently describe materials used in the "real" world, yet they do not lend themselves to characterization by many of the standard techniques appropriate only for well-defined, ordered materials. In addition to this, the use of SAXS to probe atomic order (ASAXS) in condensed media is in its infancy because it has been limited by the inherent weakness of the signals. Our initial studies[3] represent the first preliminary steps into this arena.

Small angle X-ray scattering (SAXS) has numerous applications in chemistry, metallurgy, biology, polymer science, and colloidal systems. It examines correlations at distances from 10 Å to 1000 Å and provides information about the size, morphology, and interactions of a system of particles or pores in solution or the solid state. SAXS can also be used to follow the phase transitions, crystallization, and aggregation within a system. The SAXS intensity as a function of the wave vector is due to the distance correlations of all the atoms in the particles of interest. Anomalous small angle X-ray scattering (ASAXS) refers to extensions of standard SAXS experiments in which the energy of the probing X-rays are tuned near the absorption edge of an element in the sample. By performing SAXS experiments near the characteristic absorption edge of any given atom, it is possible to vary the contrast for scattering of that particular element. This systematic variation in contrast yields the partial scattering functions of the specific atomic species. In general, the atomic scattering can be expressed as:

$$f(q,E) = f_o(q) + f'(q,E) + if''(q,E) \qquad (1)$$

where E is the energy of the probing X-rays and q is the momentum transfer ($q=4\pi\sin\theta/\lambda$, where 2θ is the scattering angle and λ is the wavelength of X-rays). The parameters f' and f" are the real and imaginary parts of anomalous dispersion. They each vary sharply at energies within 10 eV of the absorption edge. The imaginary scattering factor, f", represents the absorption of X-rays which results in photoemission of a core electron. Variation in f' is responsible for the change in contrast seen in ASAXS signals. These two quantities are related by the Kramers-Kronig relation. Typically f' is determined by measuring the energy-dependent absorption spectrum, f", and applying the Kramers-Kronig transformation. Near the absorption edge of a given atom the scattering intensity, I, varies as a function of energy or wavelength (equation 2).

$$I(q,\lambda) = I_o(q) + f'(\lambda)I_C(q,\lambda) + [f'^2(\lambda) + f''^2(\lambda)]\, I_R(q) \qquad (2)$$

Here I_o represents the nonresonant, energy-independent scattering. The cross term, I_C, reflects scattering between the specific element of interest and the remainder of the material, while I_R corresponds to the distance correlations of just the resonant scatterers.

Since f' and f" are sharply varying functions near the edge, these experiments require the highest possible energy resolution (of the order of $\Delta\lambda/\lambda=10^{-4}$) for the probing monochromatic X-rays. In these experiments we determine the small angle scattering using incoming X-rays with 4 to 5 different energies. All but one of these energies are near the absorption edge of the atom of interest. The last measurement, using X-rays whose energy is 150 eV below the edge, gives a direct measurement of the nonresonant scattering, I_o, since at this energy f' and f" are effectively zero. From these sets of data, in principle one can obtain a set of 3 to 4 differential scattering data after the subtraction of I_o. If the SAXS data as a function of energy are placed on an absolute scale, one can then use f' and f" values to obtain the partial structure factors, I_C and I_R, by least square analysis. The maximum variation in the SAXS signals near the edge depends on the maximum value of the variation of f' for a given atom. In general, the variation of f' is larger near the L_{III} edges than for the K edges. Therefore, if a transition metal ion is of interest, generally a larger weight % is necessary. This is true until higher power sources such as the Advanced Photon Source come on line in the very near future.

ASAXS is a very new technique, first reported in 1985 for the analysis of metal alloys[4]. Some review articles are available with general background information for the interested reader[5]. Only a few references exist where ASAXS has been exploited to characterize heterogeneous catalysts or supports[3,6].

EXPERIMENTAL

Bentolite L, a natural Ca^{2+}-bentonite that has been purified to removed all but 0.2 wt% Fe impurities, was obtained from Southern Clay Products. This was ion-exchanged with Cu(II), Er(III), and Yb(III) ions by stirring 1 gm clay in 100 ml of 0.1M solutions of the hydrated chloride salts overnight, followed by centrifugation, washing, and drying at room temperature. X-ray powder diffraction patterns were obtained on a Scintag PAD V instrument with Cu K_α radiation.

The powder and thick slurry samples were contained in a cell with kapton windows for SAXS measurements. The samples were measured at SAXS beamline BL 4-2 at the Stanford Synchrotron Radiation Laboratory in Stanford, CA. This beamline has a platinum coated mirror which focuses the X-rays in the horizontal direction. A 62 μRad slit upstream from this mirror defines the energy resolution of the probing X-rays at <2 eV. The reflected beam from the mirror is monochromated by a double-crystal Si(111) monochromator. The cross-sectional area of the X-ray beam, 3 mm x 1 mm, is defined by two guard slits. The beam was focused at a 20 cm long 1-dimensional position sensitive gas detector. The sample was located approximately 2.2 m upstream to the detector. Two ionization chambers, one before and one after the sample, monitored the intensity of the incident and absorbed X-rays. These monitors were also used to determine the absorption edge for the metal of interest in each of the samples. The entire beam path was under vacuum except at the sample. In this configuration the SAXS instrument can measure data in the q region from 0.008 to 0.25 $Å^{-1}$.

The acquisition time for each scattering profile was 5 minutes. During the acquisition of the scattering data, the energy of the incoming X-rays was cycled through each of the energies for 5 to 10 cycles, depending on the desired statistical precision. This procedure aided in the assessment of the stability of the sample, as well as the position of the X-ray beam. For Er-clays, an absorption edge at 8372.6 eV corresponding to the L_{III} edge of Er(III) was found. The ASAXS for the powder samples were then measured at 8100, 8355, 8368, 8370 and 8372 eV. Similar procedures were used for the remaining metal ions using their respective absorption energy edges.

RESULTS AND DISCUSSION

The dry and wet samples were analyzed by ASAXS and x-ray powder diffraction (XRD). XRD revealed that the interlayer spacings for all metal-clays increased by 4-5 Å upon hydration (formation of a wet paste) to 19.5 - 20 Å. This indicates that the interlayer has accommodated more water layers. Typically, they expand from one or two layers of water to three layers[3]. Modified Guinier analysis of the ASAXS data was used to extract the correlations for these sheet-like particles. This approach is based on the fact that the intensity of scattering for infinitely large sheets varies as q^{-2}.[7] When a Guinier analysis is performed by plotting $\ln[q^2 \cdot I(q)]$ as a function of q^2, a linear region indicates the presence of sheet-like particles. Figures 1 and 2 display the modified Guinier sheet analyses for the Cu(II)-clay and Yb(III)-clay systems, respectively. Results for Er(III)-clay were similar to Yb(III)-clay.

ASAXS intensities should increase with absorption energy if the metal ion is associated with the interlayer solvent (water, in this case), and decrease if the metal ion is associated with the solid matrix. The following discussion is provided to explain these various intensity changes. The scattering cross section of a given system is determined by the atomic scattering factor f' of the constituent atoms[8]. The f' factor includes two terms: Z, which is the number of electrons in a given atom, and a dispersion term which strongly varies only near the edge (beginning about 300 ev below the edge). Near the characteristic absorption edge f' has a minimum.

Let us consider the system of dispersed clay particles in water. The scattering from this system is determined by the number density of the particles, square of the volume of the particles, and the square of the difference in the electron densities of the particles and water. Note that the electron density of clays will always be higher than that of water. In this scenario, if the labels of interest are located within the clay lattice itself (e.g. Ni-SMM clay[3]), the difference in the electron density between the clay and the water will decrease as one approaches the absorption edge of a given metal atom. This is because the net f' value will decrease while that of the H_2O remains the same. That means that the electron density difference decreases as the energy of the probing x-rays approaches the edge and thus the scattering intensity should monotonically decrease with increasing energy[8].

On the other hand, if the metal atoms are associated with the solvent but not with the clays, then f' of the clay remains the same, but that of the solvent decreases. This means that the net electron density difference increases as one approaches the absorption edge. This will result in a monotonic increase in the scattering intensity with increasing energy as the energy of the probing x-rays approaches the absorption edge of a given atom[8].

For the same concentration of the metal atoms, the above effect will be much larger for the former case (ion-clay interaction) than that for the latter (ion-solvent interaction). This is because the signal intensity that is due to constructive interference from the scattering waves from the labels in clays is completely lost from similar atoms in solution[8].

Although there is a very slight ASAXS effect observed in the "dry" samples (Figs. 1a and 2a), the margin of error precludes us from deducing where the ions might reside. Much more of an effect is observed for the wet samples. Based on the XRD results of increased basal spacings with addition of water, we were expecting in all cases to see that the ions would be associated with the solvent (water) in the slurries. This did occur for the Cu-clay, corroborating our results from a local-environment, short-range order study by x-ray absorption spectroscopy[9]. However, neither of the Ln-clays showed an ion-solvent interaction upon increased hydration. The layer-layer correlations of the ln q^2 vs. q^2 plots clearly indicate that the Ln ions remain associated with the clay, but the decrease in scattering intensity with absorption energy indicates that these ions apparently are not fully solvated within the interlayer. This latter result was not expected and there is speculation that these ions are instead associated as hydrolyzed species with the clay surface.

The pH of each metal ion-clay slurry during ion-exchange was monitored, and were well below the hydrolysis constants of the respective ion in every case (see Table I). It has been shown that at pH's above the pK_h values, Pb(II) and Cr(III) will form oxide-hydroxide precipitates on clay surfaces[10]. Below this critical pH, these ions simply exist as exchangeable cations within the interlayer. Cu(II) behaves the same way.

Table I. Hydrolysis Study

ion-clay	pH during ion-exchange	pK_h[a]
Cu(II)	4.5	7.6
Er(III)	5.5	8.7
Yb(III)	5.5	8.0

[a] negative log of the hydrolysis constant[11].

Lanthanide ions appear to behave somewhat differently, however. Several years ago, a suite of articles reported how lanthanide sorption by montmorillonite was effected by pH, concentration, temperature, and pressure[12]. One finding reported that lanthanide hydrolysis occurs at lower pH values than are observed for aqueous solutions in the absence of clay[12c]. The presence of montmorillonite modifies the pH value at which the hydrolysis occurs, and "precipitation" commences at a lower value. This value was determined to be >5, which is in fact the case for our materials (pH 5.5). Hydrolysis is halted when the pH of the medium is acidified to <5. Er(III) and Yb(III) have similar ionic radii at 1.14 nm and 1.12 nm, respectively (coordination number 8)[11b]. Therefore, they likely have similar hydration energies and are expected to behave the same within the clay interlayer environment. It has been proposed that the specialized, localized electrostatic environment within a clay interlayer is strong enough to dissociate water ligands about a lanthanide ion, releasing OH^- ions which then react to form hydroxides[12c].

The clay surface may have an even more active role, however. With large basal spacings (ca. 20 Å), hydrated ions experience an equipotential clay surface and can interact with the clay either through hydrogen bonding (complete hydration sphere) or direct residence on the interlayer surface (partial hydration sphere)[12b]. This latter state has been the one proposed for clay suspensions and pastes. In this case, hydrolysis involves dissociation of a coordinated water molecule followed by fixation of the metal ion to the clay. Sites available for this complexation are (1) the hexagonal holes created by the basal silicate surface and (2) other surface oxygen atoms. Both of these sites have been proposed to account for an adsorption of lanthanide ions in excess of that predicted by the cation exchange capacity[12b]. Our ASAXS results appear to support the view that the ions have indeed bonded to the silicate itself, rather than simply precipitate out separately as oxide-hydroxide phases on the surface.

CONCLUSIONS

We have demonstrated that the ASAXS effect can be observed in aluminosilicate clays containing 2-3 wt% transition metal and lanthanide ions. Further, that effect can be used to elucidate how the ions solvate when the clay is hydrated to form suspensions or pastes. For instance, Cu(II) solvates within the interlayer and therefore behaves as a mobile species capable of facile ion-exchange. Under similar conditions, ASAXS has also shown that some lanthanides (at least the smaller Er(III) and Yb(III) ions) will behave in an opposite manner and instead bind to the clay lattice. A thorough understanding of the kinetics and mechanisms of heavy metal ion sorption on clay mineral surfaces is a critical issue, and the subject of recent intensive study[13]. Our results will certainly add to the view of metal ion interactions at the clay-water interface.

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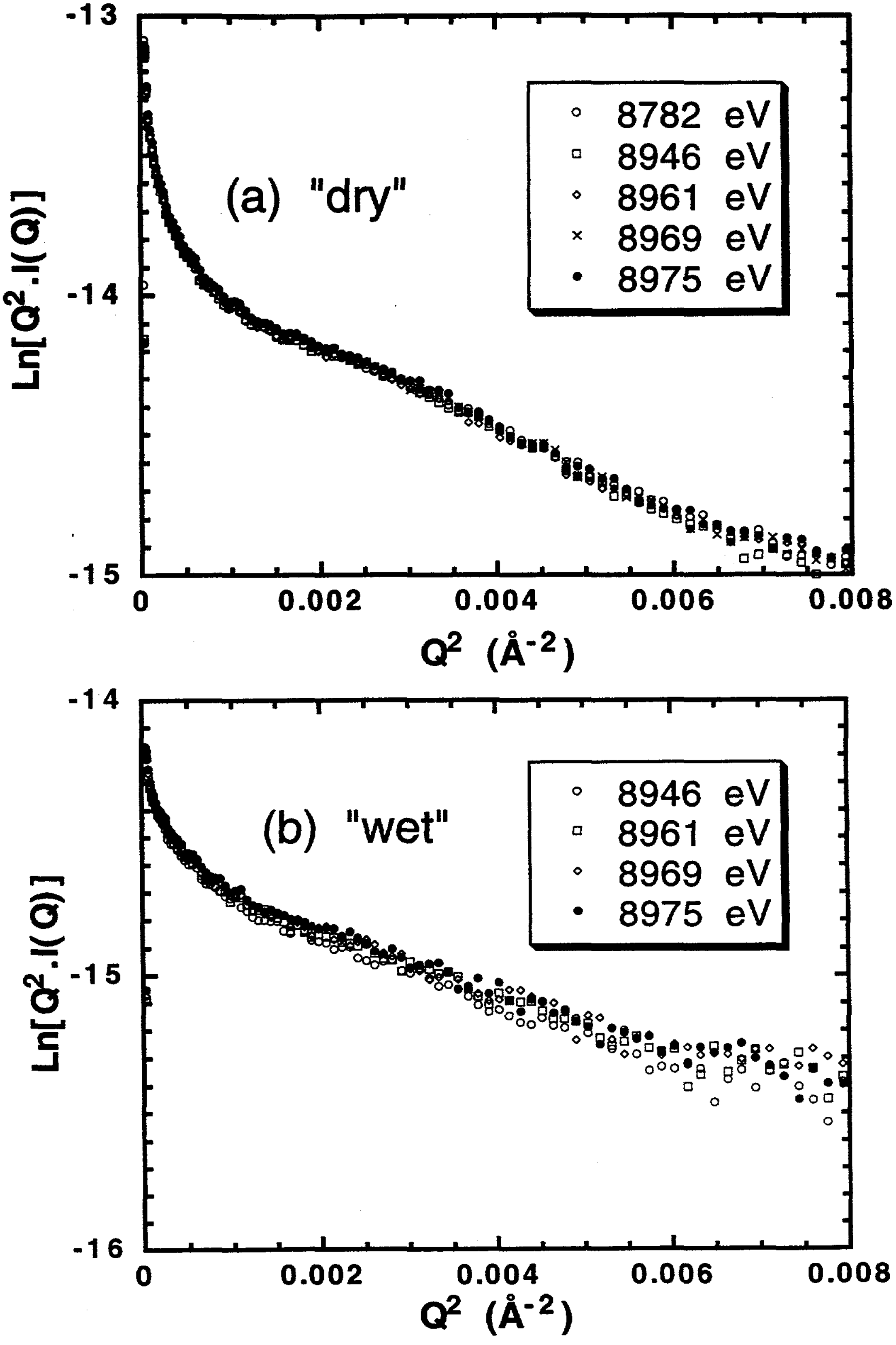

Figure 1. Modified Guinier sheet analysis of the ASAXS data for Cu(II)-clay as (a) the "dry" powder and (b) the "wet" paste.

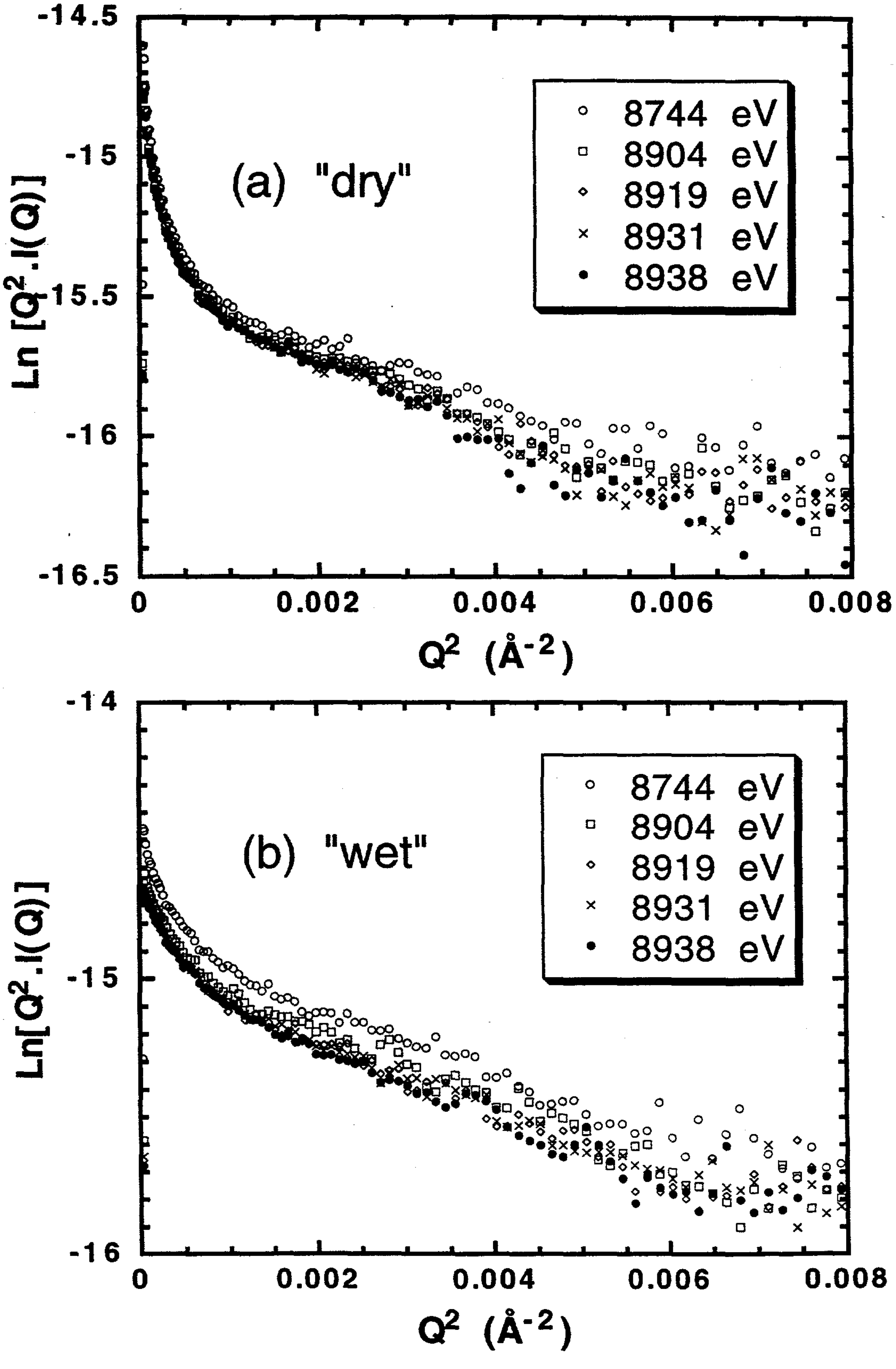

Figure 2. Modified Guinier sheet analysis of the ASAXS data for Yb(III)-clay as (a) the "dry" powder and (b) the "wet" paste.