

SANS study of dialkylsubstituted diphosphonic acids and their complexes with Ca, Fe, La,  
Th and U in toluene.

CONF-970814--

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AUG 12 1997  
OSTI<sup>1</sup>IPNS Division, Argonne National Laboratory, Argonne, IL 60439, USA<sup>2</sup>Chemistry Division, Argonne National Laboratory, Argonne, IL 60439, USA.<sup>3</sup>Department of Chemistry, Loyola University Chicago, Chicago, IL 60626, USA**Abstract**

The aggregation of di(2ethylhexyl) methane-, ethane- and butanediphosphonic acids and their complexes with various metal cations at different concentrations in toluene has been studied in detail using Small Angle Neutron Scattering. The diphosphonic acids are being employed as novel solvent extraction reagents in the Chemistry Division of ANL. These compounds exhibit extraordinarily strong affinity for actinide ions and for Fe(III). The growth of large metal-diphosphonate aggregates depends on the metal species, metal to extractant ratio, and the length of the carbon bridge between the two acid groups. Fe(III) complexes with the methane and butane (but not the ethane) bridged diphosphonic acid aggregate to form large polymeric rods at high metal to extractant ratios. Actinide ions likewise give large aggregates with di(2ethylhexyl) methanediphosphonic acid. Ca<sup>2+</sup> and La<sup>3+</sup> show only the usual formation of small 'monomeric' chelates.

**Keywords:** SANS, metal chelates, aggregation, diphosphonic acids**MASTER**

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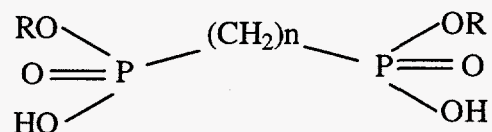
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This SANS study investigates the aggregation of chelate complexes formed by various metal ions with di(2-ethylhexyl) methanediphosphonic acid and similar compounds:



R is the 2-ethylhexyl group and n equals 1 for di(2-ethylhexyl) methanediphosphonic acid, abbreviated to H<sub>2</sub>DEH[MDP]. The corresponding ethane- and butane- compounds with n equal to 2 and 4 have also been investigated. These chelate forming molecules are of significant interest, as their extraordinarily strong affinity for actinide ions and for Fe(III) provides potential for applications as specific solvent extraction reagents. Moreover, a new extraction chromatographic resin, Dipex [1], and chelating ion exchange resin, Diphonix<sup>®</sup> [2], have been recently developed in the Chemistry Division of Argonne National Laboratory. Both systems contain immobilized diphosphonic structures.

SANS measurements were undertaken because a solvent extraction study [3] revealed that the extraction of alkaline earth metals, Fe(III) and actinide ions from aqueous HNO<sub>3</sub> solutions by H<sub>2</sub>DEH[MDP] in aromatic diluents is very complex, and that a tendency to form polymeric species is likely. Also, previous SANS experiments provided definite information on the solution structure of chelate metal complexes and the observed

aggregation of the complexes explained the related thermodynamic extraction properties [4].

The SANS experiments of this study have been performed at the time-of-flight small-angle neutron diffractometer (SAD) at IPNS [5]. To get sufficient scattering contrast, solutions in D<sub>8</sub>-toluene were used, as the extractant molecules contain high amounts of hydrogen. Prior to the scattering experiments the organic phases had been equilibrated with aqueous solutions of the metal cations at various concentrations, thus extracting different amounts of metal into the organic phase. The SANS scattering signals have been interpreted using Guinier analysis and modified Guinier analysis for rod like particles. Figures 1 and 2 show representative plots obtained from the H<sub>2</sub>DEH[MDP]-Fe<sup>3+</sup> system. These data belong to an extraction series where Fe<sup>3+</sup> has been extracted from 0.1 M HNO<sub>3</sub>. Fig.1 shows clearly the increase in the size of the scattering objects with increasing Fe<sup>3+</sup> concentration. This tendency is observed in all experiments on the H<sub>2</sub>DEH[MDP]-Fe<sup>3+</sup> system. The analysis of the same data with Guinier approximation for rod like particles (Fig. 2) yields a constant radius for the rod of 7 ± 0.1 Å. At higher concentrations of Fe<sup>3+</sup> the scattering curve bends into the limiting intensity at lower scattering vectors, corresponding to an increase in the rod length. When more and more metal is brought into the organic phase, it attaches itself to the available terminal 'handles' of the existing rod-like polymers.

The evaluation of molecular mass using the Guinier approximation reveals that H<sub>2</sub>DEH[MDP] exists as a dimer if no metal cations are present. The aggregation number of H<sub>2</sub>DEH[MDP] always increases upon extraction of any of the metal cations. Ca<sup>2+</sup> and La<sup>3+</sup> yield an aggregation number close to 4 with a negligible concentration dependence.

For Fe(III), Th(IV) and, to a lesser degree, U(VI), much larger aggregates are observed (Fig. 3).

The SANS experiments show different results for the di(2ethylhexyl) ethane- and butanediphosphonic acids, abbreviated as H<sub>2</sub>DEH[EDP] and H<sub>2</sub>DEH[BuDP]. It can be concluded that H<sub>2</sub>DEH[EDP] exists as a hexamer. H<sub>2</sub>DEH[BuDP] yields an aggregation number between 4 and 5. The aggregation number of H<sub>2</sub>DEH[EDP] is in most cases only slightly affected by metal extraction. H<sub>2</sub>DEH[BuDP] shows extraction reactions similar to H<sub>2</sub>DEH[MDP] with a significant increase in aggregate size at higher concentrations of Fe(III).

We thank D. G. Wozniak of the IPNS Division for assistance on the SANS experiments. This work benefited from the use of the Intense Pulsed Neutron Source. This facility is funded by BES-Materials Science, US Department of Energy, under contract W-31-109-ENG-38.

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### Figure Captions

Fig. 1: SANS Data of H<sub>2</sub>DEH[MDP] / Fe<sup>3+</sup> complexes in D-toluene. The size of the aggregates increases with increasing iron concentration.

Fig. 2: SANS Data of H<sub>2</sub>DEH[MDP] / Fe<sup>3+</sup> complexes plotted for analysis in Guinier approximation for rod like particles.

Fig. 3: Aggregation number of H<sub>2</sub>DEH[MDP] complexes with Fe(III) and actinide ions. The aggregation number increases with increasing concentrations of metal in the aqueous phase.

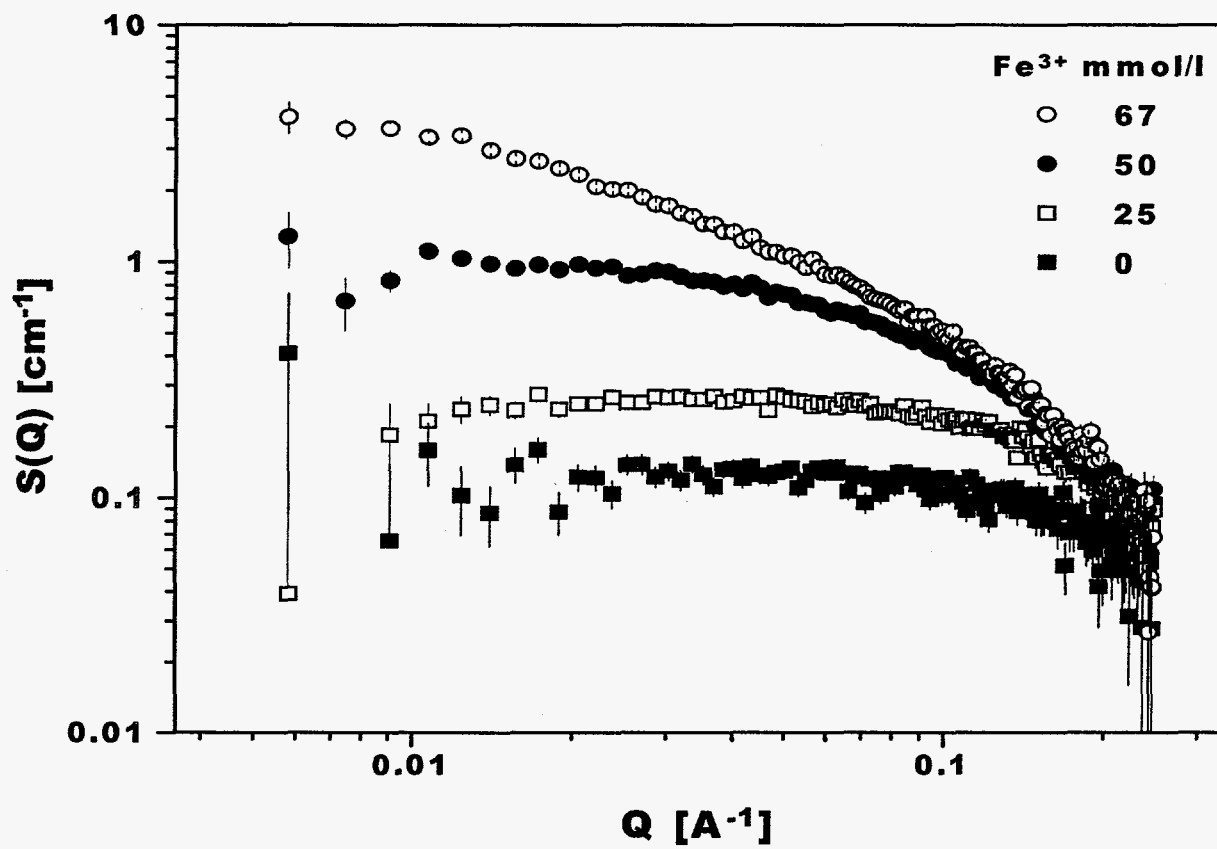


Fig. 1

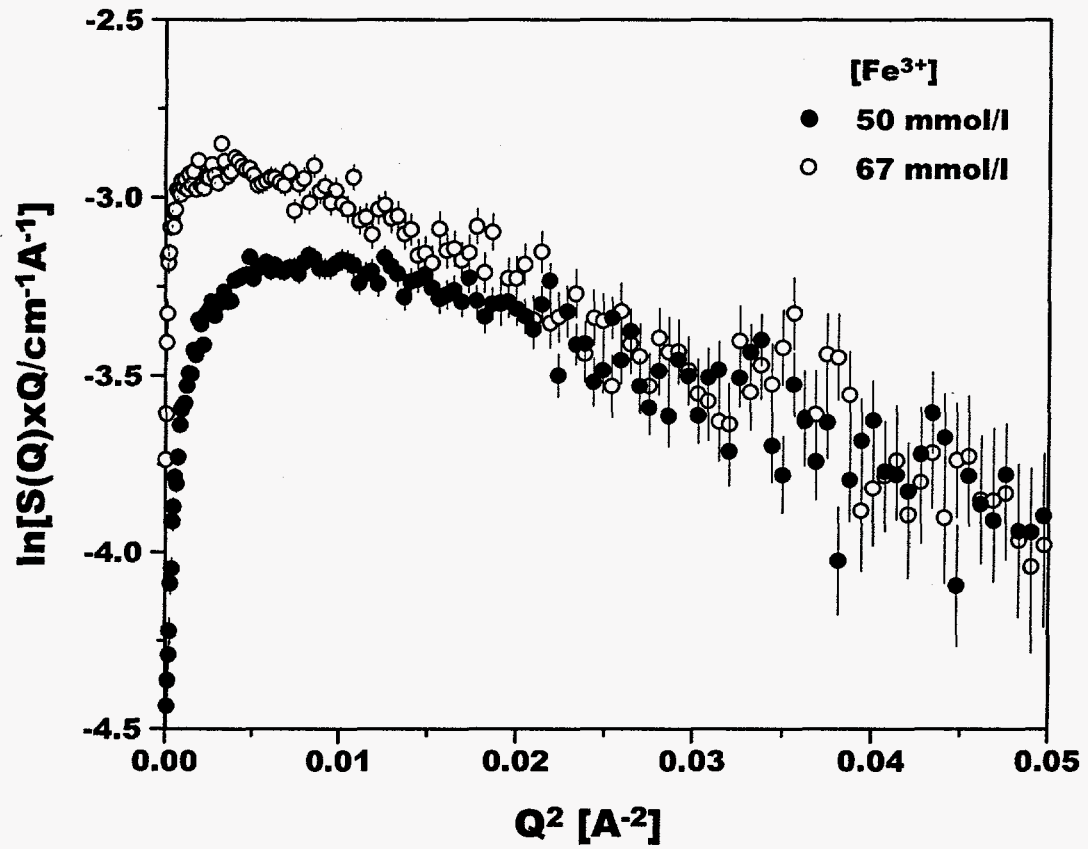


Fig. 2

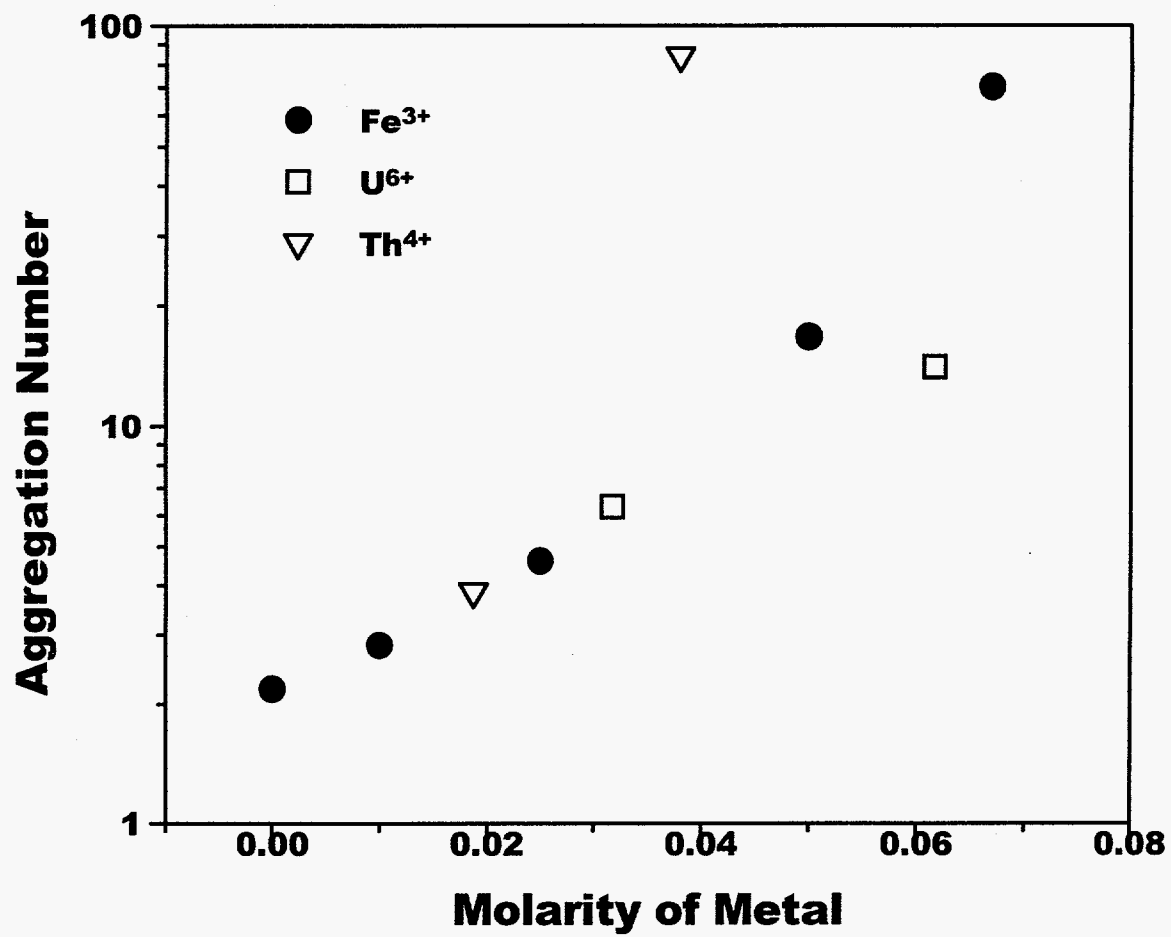


Fig. 3