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Aggregation and Metal Ion Extraction Properties of Novel, Silicon-Substituted Alkylenediphosphonic Acids*

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In conjunction with efforts to develop novel actinide extractants exhibiting solubility in supercritical carbon dioxide, the effect of adding silicon-based functionalities to diphosphonic acids has been investigated. Specifically, a series of silyl-substituted diphosphonic acids has been prepared and characterized, and their aggregation and metal ion extraction properties compared with alkyl-substituted diphosphonic acids, reagents previously demonstrated to be effective extractants of actinides from acidic aqueous media into various organic solvents. In addition, the influence of the number of methylene groups bridging the phosphorus atoms of the diphosphonic acids on their extraction behavior has been investigated. Variations in the extraction behavior of the compounds arising from differences in the number of bridging methylene groups have been shown to be attributable to a combination of factors, in particular, the aggregation state of the ligand, the size of the chelate rings formed upon complexation, the basicity of the phosphoryl group and the relative acidities of the ligands.

INTRODUCTION

Partial esters of diphosphonic acids in organic solvents have been shown to be efficient metal ion extractants, exhibiting a particular affinity for tri-, tetra- and hexavalent actinides and Fe(III) [1]. In previous work, which grew out of an effort to synthesize supercritical CO_2-soluble

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diphosphonic acid ligands, a series of silyl-substituted diphosphonic acids was investigated to determine the effect of incorporating a silicon functionality into a diphosphonic acid. While the incorporation of the silyl functionality was shown to have a relatively minor effect on the aggregation and metal ion extraction properties of the ligands, a more profound effect on these properties was observed as the length of the alkyl chain bridging the phosphorus atoms was varied. This work represents the first step toward understanding this effect, as part of a broader effort to determine the relationship between structure and function in diphosphonic acids.

EXPERIMENTAL

All materials, instrumentation and experimental conditions used in this study were as previously described [2, 3]. The aggregation states of the ligands in toluene at 25°C were determined by vapor pressure osmometry using a Jupiter Model 833 vapor pressure osmometer. Infrared spectra were obtained by taking 64 scans at 2 cm^{-1} resolution on a Mattson Genesis Series FTIR spectrometer. ^{31}P NMR spectra were collected on a Varian 400 MHz spectrometer, with chemical shifts reported relative to an external 85% H_3PO_4 reference. Duplicate measurements showed that the reproducibility of the distribution ratio measurements was generally within five percent, although the uncertainty interval was higher for the highest and lowest D values ($D>10^3$, or $D<10^{-3}$).

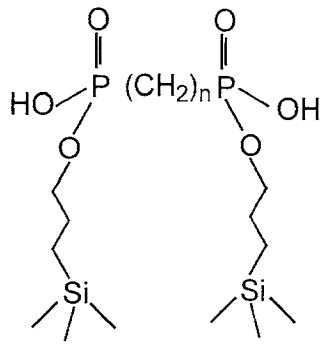

Figure 1. General Structure of Silyl-Substituted Diphosphonic Acids.

RESULTS AND DISCUSSION

Aggregation

The aggregation state of the silyl-substituted diphosphonic acids (Figure 1) was found to vary dramatically as a function of the number of methylene groups bridging the phosphorus atoms. As can be seen in Table 1, the ligands with an odd number of bridging methylene groups exist as dimers, while those with an even number tend to form more highly aggregated species. While the origin of this even/odd effect is not fully understood in these systems, it appears to be due to the "zig-zag" pattern adopted by the alkyl chain separating the phosphorus atoms. This affects the orientation of the P=O and P-OH groups of the ligands and changes the geometry of the hydrogen bonded aggregates which can be formed between the ligand molecules. As is

observed with normal "straight chain" alkanes, this even/odd effect also manifests itself in the melting points of the ligands, with the ligands containing an even number of bridging methylene groups exhibiting higher than expected melting points (Table 1). Molecular mechanics calculations are currently being performed to determine the most energetically stable conformations of these ligand aggregates.

Table 1. Properties of Silyl-Substituted Diphosphonic Acids

compound	n[1]	aggregation	δ ^{31}P NMR	P=O str. (cm^{-1})	m.p. (°C)
H_2DTMSP[MDP]	1	dimeric	19.97	1230	32-34
H_2DTMSP[EDP]	2	hexameric	31.43	1212	90-92
H_2DTMSP[PrDP]	3	dimeric	33.51	1197	46-47
H_2DTMSP[BuDP]	4	trimeric/heximeric	34.41	1194	75-78
H_2DTMSP[PDP]	5	dimeric	34.74	1192	N/A
H_2DTMSP[HDP]	6	trimeric/heximeric	34.38	1192	N/A

[1]number of bridging methylene groups

^{31}P NMR and Infrared Spectroscopy

Due to the electron withdrawing effect of one phosphoryl group of the diphosphonic acid on the other, the P=O basicity and P-OH acidity of these ligands are expected to vary with the number of bridging methylene groups separating the phosphorus atoms. This is illustrated clearly in the ^{31}P NMR and infrared spectroscopy of these ligands. The ^{31}P chemical shifts observed for these ligands are essentially the same as those observed for the corresponding monophosphonates in which the second phosphorus atom has been replaced by an electronegative substituent, such as chlorine [4]. As this electronegative group is separated from the phosphorus atom by an increasing number of methylene groups, the electron withdrawing effect diminishes and the P=O basicity increases, while the P-OH acidity decreases. The magnitude of this difference is expected to be the greatest between the ligands with one and two bridging methylene groups, for which the difference in ^{31}P chemical shift is the greatest. When more than three methylene groups bridge the two phosphorus atoms, the ^{31}P chemical shift observed is essentially the same as that for a monophosphonate, where the second phosphorus atom has been replaced by an alkyl substituent. Beyond this point, the P=O basicity and P-OH acidity are expected to remain constant with the incorporation of more bridging methylene groups, as evidenced by the constant ^{31}P chemical shift observed for the ligands with four or more bridging methylene groups. Attempts are currently underway to determine the pK_a's of a series of analogous water-soluble, substituted diphosphonic acids to provide a more quantitative description of this effect.

A similar trend is observed in the infrared spectra of this series of ligands. As more methylene groups are incorporated between the phosphorus atoms of these ligands the P=O stretching vibration is shifted to lower energy (Table 1). As in the ^{31}P NMR spectra, the largest difference in energy is observed between the phosphoryl stretching bands of the ligands with one and two bridging methylene groups. The position of the stretching bands for the ligands with more than

three bridging methylene groups are essentially identical. It should be noted that the position of the phosphoryl stretching band is very sensitive to hydrogen bonding. However, the same trend is also observed for the analogous series of tetraethyl diphosphonates, which do not form hydrogen bonded aggregates, suggesting that this trend is primarily due to the electronic effect of phosphoryl groups on each other.

Solvent Extraction

Figure 2a shows the nitric acid dependent extraction of Am(III) by 0.01M solutions of the extractants in *o*-xylene. (For brevity, in this section, the ligands are denoted by their number of bridging methylene groups in parentheses.) Because a detailed investigation of the solvent extraction properties of this series of ligands has been described previously [2,3], for the purposes of the present discussion, it is sufficient to note that the extraction of Am(III) clearly exhibits the general trends observed as the number of methylene groups separating the phosphorus atoms is varied. A slope of negative three is exhibited by the acid dependencies of all of the extractants over at least part of the acid concentration range studied. This indicates that three protons are displaced from the extractant aggregates upon metal ion complexation, consistent with the plus three charge of the Am(III) cations. At higher acid concentrations, the extractants with more than three bridging methylene groups tend to exhibit acid dependency plots with a less negative or even positive slope. This suggests an increased importance of extraction by the neutral (fully protonated) extractant and provides evidence to support the reduced acidity of these ligands suggested by the ^{31}P NMR and infrared spectroscopy experiments (*vide supra*).

Figures 2b and 2c show the extractant dependencies for Am(III) extraction by the series of silyl-substituted diphosphonic acid ligands. The plots for the ligands with an odd number of bridging methylene groups exhibit extractant dependency slopes of two, suggesting that two dimeric ligand units participate in the extraction of each Am(III) cation. The efficiency of Am(III) extraction decreases as the number of bridging methylene groups incorporated into the ligand increases from 1 to 3 to 5, even though the basicity of the phosphoryl oxygen increases over the same series. This suggests that the chelate effect is the dominant factor in determining the differences in the efficiency of metal ion extraction observed for this series of ligands. The six-membered rings formed upon complexation of metal ions by (1) is favored over the larger rings possible upon complexation by (3) or (5). Even though a true chelate effect is not expected to be present when considering the larger ring sizes possible upon complexation of metal ions by (3) and (5), the higher efficiency of metal extraction by (3) may be due to a small entropic advantage due to the closer proximity of two phosphoryl groups.

The ligands with an even number of bridging methylene groups exhibit Am(III) extraction dependency plots with slopes less than two, suggesting the importance of extraction by a single, highly aggregated species. Ligand (2) exhibits an extractant dependency slope of one, except at the lowest extractant concentrations, suggesting that Am(III) is primarily extracted by a single hexameric aggregate of (2). Ligands (4) and (6) exhibit extractant dependency slopes that are close to two at lower concentrations and decrease slightly as the extractant concentration increases. This agrees with the vapor pressure osmometry data, which suggests that these ligands exist as an equilibrium mixture of trimeric and hexameric species in toluene. Thus, at lower extractant concentrations, Am(III) is extracted by two trimeric aggregates of (4) or (6), while at higher extractant concentrations, extraction by a single hexameric aggregate becomes

important. Additionally, since fitting of the vapor pressure osmometry data suggests that (6) tends to more highly aggregated than (4) at a given extractant concentration, the slightly more efficient extraction of Am(III) observed for (6) versus (4) suggests that extraction by this single hexameric aggregate is more efficient than extraction by two trimeric species. Furthermore, extraction of Am(III) by (4) and (6) is more efficient than extraction by the dimeric ligands (3) or (5) under analogous conditions, suggesting that extraction by the single hexameric species is more efficient than extraction by two dimeric extractant units, except in the case of (1), where the chelate effect is the dominant factor in determining extraction efficiency.

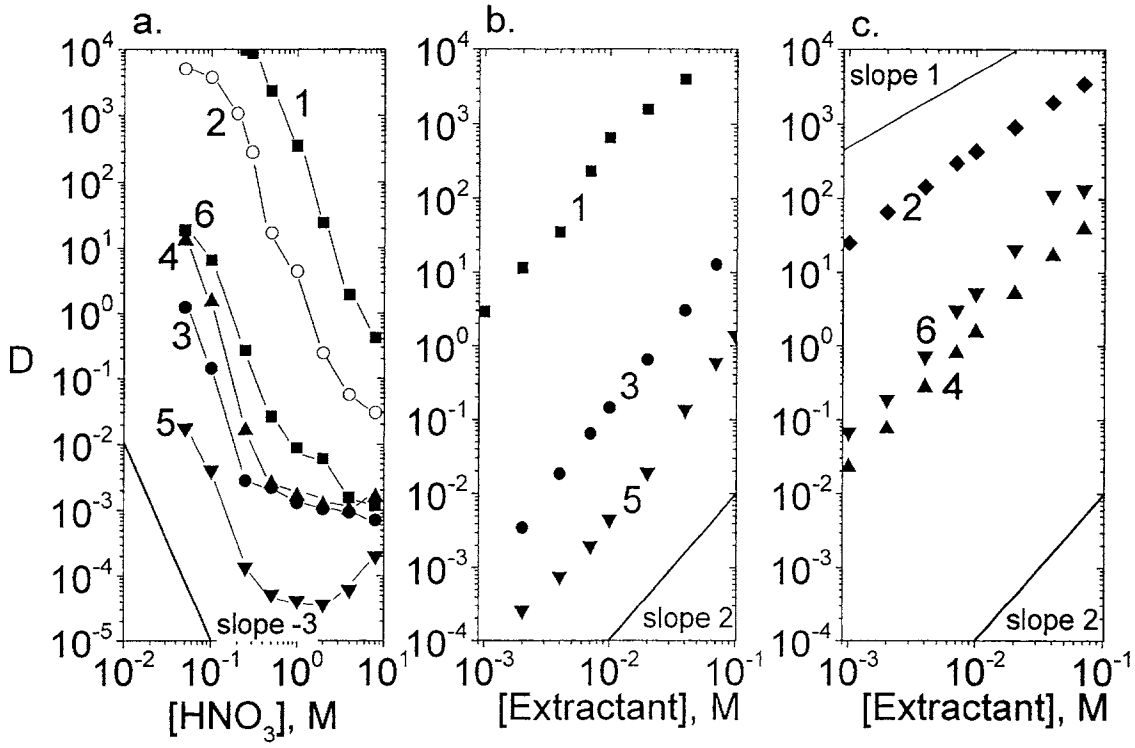

Figure 2. Solvent extraction of Am(III) from aqueous nitric acid by silyl-substituted diphosphonic acids in o-xylene. a. Acid dependencies for the extraction of Am(III) by 0.01 M extractant in o-xylene. b. Extractant dependencies for Am(III) extraction from 1.0 M (1) or 0.1 M HNO_3(3 and 5) by silyl-substituted diphosphonic acids with odd numbers of bridging methylene groups. c. Extractant dependencies for Am(III) extraction from 0.1 M HNO_3 by silyl-substituted diphosphonic acids with even numbers of bridging methylene groups. (Numbers on plots refer to the number of bridging methylene groups).

Comparison of Silyl-Substituted and 2-Ethylhexyl-Substituted Diphosphonic Acids

Vapor pressure osmometry, solvent extraction and ^{31}P NMR and infrared spectroscopy experiments show that incorporation of a silyl functionality into a diphosphonic acid does not adversely affect its metal ion extraction properties relative to analogous alkyl-substituted diphosphonic acids. Silyl-substituted diphosphonic acids exhibit the same aggregation behavior as and typically extract metal ions 2-3 times more efficiently than their 2-ethylhexyl-substituted

analogues [2,3]. ^{31}P NMR and infrared spectroscopy experiments suggest that this increased extraction efficiency may be due to a slightly higher P=O basicity in the silyl-substituted diphosphonic acids [3].

CONCLUSIONS

The extraction of metal cations by a series of silyl-substituted diphosphonic acids has been shown to be affected by a number of factors, including the aggregation state of the ligand, the size of the chelate rings formed upon complexation, the basicity of the phosphoryl group and the relative acidities of the ligands. Metal ion extraction is most efficient when one methylene group bridges the two phosphorus atoms of the partially esterified diphosphonic acid extractant, due to the stability of the six-membered chelate rings formed upon metal ion complexation. As more bridging methylene groups are added, metal ion extraction tends to become less efficient and the aggregation state of the ligand becomes a more important factor in determining this efficiency. The incorporation of a silyl functionality into diphosphonic acids does not adversely affect the solvent extraction properties relative to analogous alkyl-substituted diphosphonic acids, with the silyl-substituted ligands typically extracting metal ions 2-3 times more efficiently, presumably due to the slightly higher basicity of their P=O groups.

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