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Aggregation, Metal Ion Extraction, and Solubility Properties of Silyl-Substituted Alkylenediphosphonic Acids

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ABSTRACT

Partially esterified alkylenediphosphonic acids were shown to be effective solvent extraction reagents for the removal of actinide cations from acidic aqueous solutions into conventional organic solvents. As a first step in an effort to design diphosphonic acid extractants that are soluble in supercritical carbon dioxide, we prepared and characterized a novel series of silyl-substituted alkylenediphosphonic acids. The aggregation of these extractants in toluene at 25°C was studied by vapor pressure osmometry. Their solvent extraction chemistry was investigated by employing radiotracers to determine the distribution ratios for selected metal ions

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between an acidic aqueous phase and an organic phase containing the diphosphonic acid extractant. To determine the effect of incorporating a silicon functionality into diphosphonic acids, the aggregation and solvent extraction properties of the silyl-substituted alkylenediphosphonic acids were compared with those of the conventional alkyl-substituted di(2-ethylhexyl) alkylenediphosphonic acids. The aggregation and solvent extraction properties of these ligands were shown to vary dramatically as a function of the number of methylene groups bridging the phosphorus atoms of the extractant. Factors including aggregation, P=O basicity, POH acidity, and chelate-ring size were explored to explain features of the solvent extraction data. Additionally, the solubility of the silyl- and alkyl-substituted ligands in supercritical carbon dioxide was studied.

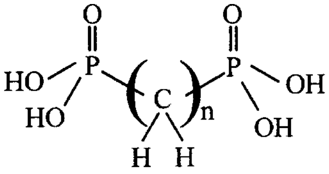
Key Words: Diphosphonic acids; Silyl-substituted; Supercritical carbon dioxide.

INTRODUCTION

Diphosphonic acids have been extensively studied as metal ion complexants[1–5] and, upon appropriate substitution, have provided the basis for powerful metal ion extractants[6–8] and a variety of novel ion-exchange[9–16] and extraction chromatographic[17] materials. Previous work in this laboratory demonstrated that these compounds form remarkably stable complexes in acidic media with a variety of metal ions, such as lanthanides, actinides, and Fe(III). The high affinity of diphosphonic acids for these cations is attributed to their ability to chelate metal ions through either phosphoryl or ionized phosphonic acid groups.[5,6] During the past several years, supercritical carbon dioxide ($SCCO_2$) received increased attention as an "environmentally benign" alternative to conventional organic solvents.[18] Unlike many organic solvents, CO_2 does not decompose into ozone-depleting fragments or promote the generation of photochemical smog. In addition, the use of CO_2 can lead to reduced waste streams, since solutes dissolved in $SCCO_2$ can be recovered by simply reducing the applied pressure. The CO_2 then reverts to the gas phase and can be collected, repressurized, and reused, while the dissolved solutes can be collected as a liquid or solid residue. $SCCO_2$ also offers a number of other significant advantages as a diluent, such as low cost, ready availability, relative ease of handling (critical temperature and pressure easily achievable with standard high-pressure equipment), low viscosity, and high diffusivity.[18]

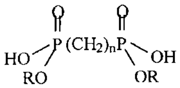
Coupling the complexing power of diphosphonic acids with the unique solvent properties of $SCCO_2$ could provide a powerful tool for separating metal ions from a variety of media. Unfortunately, neither unsubstituted diphosphonic acids nor the alkyl-substituted diphosphonic acids reported to date [e.g., P,P′-di(2-ethylhexyl) alkylenediphosphonic acids] are sufficiently soluble in unmodified $SCCO_2$ to be practical metal ion extractants in this medium.[19] Although the low-solvent power of $SCCO_2$ can be improved through the addition of modifiers or increasing the applied pressure, these approaches are not always effective or desirable. For these reasons, a lot effort has been directed toward the development of metal ion complexants incorporating "CO_2-philic" substituents, such as fluorine atoms or silicone polymer functionalities.[20–31]

Recent work in our laboratory focused on the preparation of diphosphonic acid derivatives incorporating various silicone and fluorine functionalities for possible application in $SCCO_2$.[32] Alkylenediphosphonic acids contain two major sites that can be functionalized to modify their solubility properties: the alkylene bridge separating the phosphorus atoms and the acidic POH groups (Structure I). In our work, the functionalization of both of these sites was explored. This article details the conventional liquid–liquid solvent extraction, aggregation, and $SCCO_2$ solubility properties of one series of ligands that has been synthesized in our laboratory in an attempt to provide some insight into how diphosphonic acids can be functionalized to maximize their utility as metal ion extractants in $SCCO_2$.

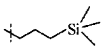


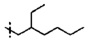
Structure I

In this article, the liquid–liquid solvent extraction, aggregation, and $SCCO_2$ solubility properties of a series of di[3-(trimethylsilyl)-1-propyl] esterified alkylenediphosphonic acids, in which the length of the alkylene chain bridging the phosphorus atoms is varied, are discussed and compared to those of an analogous series of di(2-ethylhexyl) esterified diphosphonic acids (Structure II). The 3-trimethylsilyl-1-propyl group was chosen to determine the feasibility of incorporating a silicon functionality into a diphosphonic acid because the corresponding alcohol was commercially available and could be used to esterify diphosphonic acids using a well characterized method.[33–35] Additionally, the separation of the trimethylsilyl (TMS) group from the rest of the molecule provides optimal chemical stability and synthetic accessibility.[36] While the addition of the TMS group was not expected to significantly increase the solubility of diphosphonic acids in $SCCO_2$,[19] information gathered on this group of extractants was expected to provide valuable information on the effect of incorporating silicon functionalities into diphosphonic acids on their aggregation and metal ion extraction properties.



Structure II





n	R = 3-trimethylsilyl-1-propyl	R = 2-ethylhexyl
1	H_2DTMSP[MDP]	H_2DEH[MDP]
2	H_2DTMSP[EDP]	H_2DEH[EDP]
3	H_2DTMSP[PrDP]	-
4	H_2DTMSP[BuDP]	H_2DEH[BuDP]
5	H_2DTMSP[PDP]	-
6	H_2DTMSP[HDP]	-

Previous work shows that the aggregation and solvent extraction properties of these ligands varies dramatically as the length of the alkylene chain bridging the phosphorus atoms increases.[37,38] Given recent reports of differences in the $SCCO_2$ solubility of the monomeric and dimeric forms of various carboxylic acids,[39,40] information relating diphosphonic acid structure to aggregation behavior is expected to be of value in efforts to improve the solubility of this family of extractants in $SCCO_2$.

EXPERIMENTAL

Materials

All extractants employed in this study were synthesized and characterized as described previously[33–35] and were shown to be greater than 97% pure by potentiometric titration with standard base (J.T. Baker Chemical Co.). Solutions used in the vapor pressure osmometry experiments were prepared by dissolving a know mass of extractant in a know mass of toluene (Photrex Reagent, J.T. Baker Chemical Co.). Aqueous solutions were prepared using water from a Milli-Q2 purification system and Ultrex Reagent nitric acid

(J.T. Baker Chemical Co.). Organic solutions used in the solvent extraction experiments were prepared by dissolving a known mass of the extractant in enough *o*-xylene (Aldrich Chemical Co.) to achieve the desired molarity (volumetric flask). ^{241}Am was obtained from ANL stocks. Liquid CO_2 (99.9995% min, SFC/SFE grade) was purchased from AGA Gas, Incorporated. Glass wool (0.0009 to 0.0012-inch diameter) was obtained from Fisher Scientific Company.

Measurements

Vapor pressure osmometric and distribution ratio measurements were made using the techniques, instrumentation, and procedures described previously.[41] The distribution ratio D was calculated as the ratio of the activity of a radiotracer between an *o*-xylene solution of the extractant and an aqueous nitric acid solution. Typically, a solution of the extractant in *o*-xylene was twice pre-equilibrated with an equal volume of an aqueous nitric acid solution. A 500-μL aliquot of the pre-equilibrated organic phase was then vortexed with an equal volume of a fresh aqueous phase spiked with 3 to 5 μL of radiotracer dissolved in aqueous HNO_3. Preliminary experiments showed that 5 minutes of vortexing was adequate for the attainment of equilibrium. The samples were then centrifuged to facilitate phase separation and 200 μL of each phase were taken for radiometric measurements by a Packard Cobra Auto Gamma counter. Duplicate measurements showed that the reproducibility of the distribution ratio measurements was generally within 5%, although the uncertainty interval was higher for the highest and lowest D values ($D > 10^3$, or $D < 10^{-3}$).

Infrared spectra of 0.10-M solutions of the ligands in CCl_4 were obtained by taking 64 scans at 2-cm^{-1} resolution on a Mattson Genesis Series FTIR spectrometer. CCl_4 (J.T. Baker Chemical Co.) in a liquid cell with NaCl windows was used as the background. ^{31}P NMR spectra of the ligands were recorded in $CDCl_3$ (Aldrich Chemical Co.) by collecting 100 scans on a Varian 400 MHz spectrometer. Chemical shifts are reported relative to an external 85% H_3PO_4 reference. The solubilities of the ligands in $SCCO_2$ were determined using an ISCO SFX System 2130 with two model 260D syringe pumps and an SFX 220 extractor with a coaxially heated (60°C) adjustable restrictor (Fig. 1). Solubilities were determined at 60°C and 250 bar. The CO_2 syringe pump was cooled to 5°C by a water jacket connected to a Neslab recirculating water bath. A known mass ($\backsim$400 mg) of extractant was placed in a 9-mL

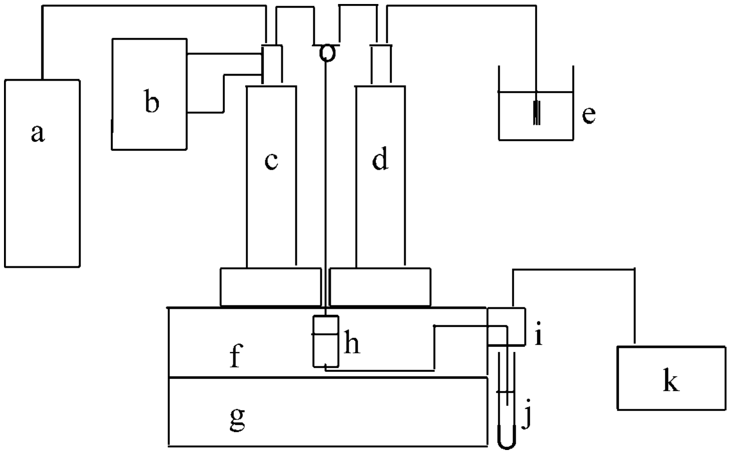


Figure 1. ISCO SFX System 2130. a. Liquid CO_2. b. Water bath (5°C). c. Syringe pump A (CO_2). d. Syringe pump B (modifier). e. Modifier reservoir. f. Extraction chamber. g. Temperature and pressure control. i. Adjustable restrictor. j. Collection vial, k. Restrictor temperature control.

high-temperature crystalline polymer sample cartridge with 2-μm frits (ISCO) containing glass wool to reduce the dead volume. The sample cartridge was charged with CO_2 and a 15-minute static extraction step was allowed to elapse. While the pressure and temperature were maintained at 250 bar and 60°C, respectively, the restrictor was opened to achieve a flow rate of 2.30 ± 0.20 mL/minute, and the eluent collected at 3.00-mL intervals into preweighed, dried borosilicate glass sample vials containing hexane (Fisher Scientific Co.). The hexane was then removed by rotoevaporation at 40°C and the sample vials were placed in a vacuum oven at 60°C for 18 hours. The sample vials were then allowed to cool to room temperature in a desiccator, and the mass of extractant recovered was determined gravimetrically. The sample cartridges were also dried *in vacuo* at 60°C for 18 hours and weighed to allow the determination of mass balance. In all cases, good mass balances (±5%) were obtained. Duplicate experiments showed that reproducibility was generally within 5%, unless the flow rate was varied dramatically. Therefore, care was given to maintain a constant flow rate during the course of a given experiment as well as over the entire series of experiments.

RESULTS AND DISCUSSION

Aggregation

The aggregation state of partially esterified alkylenediphosphonic acids in nonpolar diluents varies dramatically as a function of the number of methylene groups bridging the phosphorus atoms. As can be seen in Table 1, in toluene at 25°C, the extractants 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 alkylene 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 that can be formed between the extractant molecules. Molecular mechanics calculations are currently being performed to determine the most energetically stable conformations of these hydrogen-bonded aggregates.

^{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.[42,43] This is illustrated clearly in the ^{31}P NMR and infrared spectroscopy of these ligands (see Table 1). The ^{31}P chemical shifts observed for these ligands are essentially the same as those

Table 1. Selected properties of alkylenediphosphonic acid symmetric partial esters.

n[a]	Aggregation	$\delta\ ^{31}$P NMR of DEH ester	$\delta\ ^{31}$P NMR of DTMSP ester	P═O str. (cm^{-1}) of DEH ester	P═O str. (cm^{-1}) of DTMSP ester
1	Dimeric	19.9	20.0	1238	1230
2	Hexameric	31.1	31.4	1214	1212
3	Dimeric	N/A	33.5	N/A	1197
4	Trimeric/hexameric	34.1	34.4	1200	1194
5	Dimeric	N/A	34.7	N/A	1192
6	Hexameric	N/A	34.4	N/A	1192

[a] Number of bridging methylene groups.

observed for the corresponding monophosphonates, in which the second phosphorus atom has been replaced by an electronegative substituent, such as chlorine.[44] 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 essentially 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 (see 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,[44] which do not form hydrogen-bonded aggregates, suggesting that this trend is primarily due to the electronic effect of phosphoryl groups on each other.

It should be noted, that in the discussion of the acidity of these extractants, the term P—OH acidity refers to the pK$_a$ of the most acidic proton. Solvent extraction,[6,15,16,37,38] infrared spectroscopy,[41] vapor pressure osmometry,[41] and small-angle neutron scattering data[45,46] suggests the complexation of metal cations by these extractants does not disrupt the aggregation of the extractant under the conditions used for the solvent extraction experiments discussed in this article. In these extracted complexes, the individual diphosphonic acid molecules are either mono-deprotonated or fully protonated. Data for the pK$_a$'s of analogous series of unsubstituted diphosphonic acids[47] and dicarboxylic acids[48] show that the pK$_a$ of the most acidic proton increases as the number of methylene groups bridging the two acidic groups (POOH or COOH) increases. However, the pK$_a$ of the second acidic proton is often observed to remain the same or even decrease as the acidic groups are separated by longer alkylene chains.

Solvent Extraction

Figure 2a shows the nitric acid dependent extraction of Am(III) by 0.01M solutions of the silyl-substituted extractants in *o*-xylene. Because a detailed investigation of the solvent extraction properties of this series of ligands has been described previously,[37,38] 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 -3 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 $+3$ 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 c 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 aggregates 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 may be the dominant factor in determining the differences in the efficiency of metal ion extraction observed for this series of dimeric ligands, with the six-membered rings formed upon complexation of metal ions by H_2DTMSP[MDP] expected to be considerably more stable than the larger rings possible upon complexation by H_2DTMSP[PrDP] or H_2DTMSP[PDP]. However, it should also be noted that the acidity of the ligands is expected to decrease over this same series and may also play an important role in determining the efficiency of metal ion extraction.

The ligands with an even number of bridging methylene groups exhibit Am(III) extraction dependency plots with slopes less than 2, suggesting the importance of extraction by a single, highly aggregated species.

H_2DTMSP[EDP] exhibits an extractant dependency slope of 1, except at the lowest extractant concentrations, suggesting that Am(III) is primarily extracted by a single hexameric aggregate. H_2DTMSP[BuDP] and H_2DTMSP[HDP] exhibit extractant dependency slopes that are close to 2 at

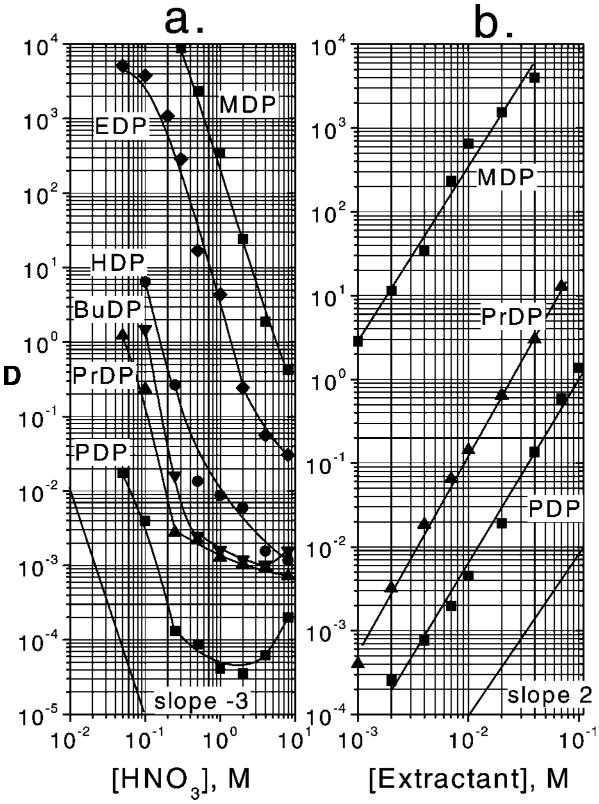


Figure 2. a. Nitric acid dependency for the extraction of Am(III) by 0.01 M solutions of H_2DTMSP[MDP], H_2DTMSP[EDP], H_2DTMSP[PrDP], H_2DTMSP[BuDP], H_2DTMSP[PDP], and H_2DTMSP[HDP] in *o*-xylene. b. Extraction of Am(III) from 1.0-M HNO_3 by H_2DTMSP[MDP] and from 0.1-M HNO_3 by H_2DTMSP[PrDP] and H_2DTMSP[PDP] in *o*-xylene as a function of the extractant concentration in the organic phase. c. Extraction of Am(III) from 0.1-M HNO_3 by H_2DTMSP[EDP], H_2DTMSP[BuDP] and H_2DTMSP[HDP] in *o*-xylene as a function of the extractant concentration in the organic phase. d. Extraction of Am(III) from 1.0-M HNO_3 by (■)H_2DTMSP[MDP], (●)H_2DEH[MDP], (◆)H_2DTMSP[EDP], and (▼)H_2DEH[EDP] in *o*-xylene as a function of the extractant concentration in the organic phase.

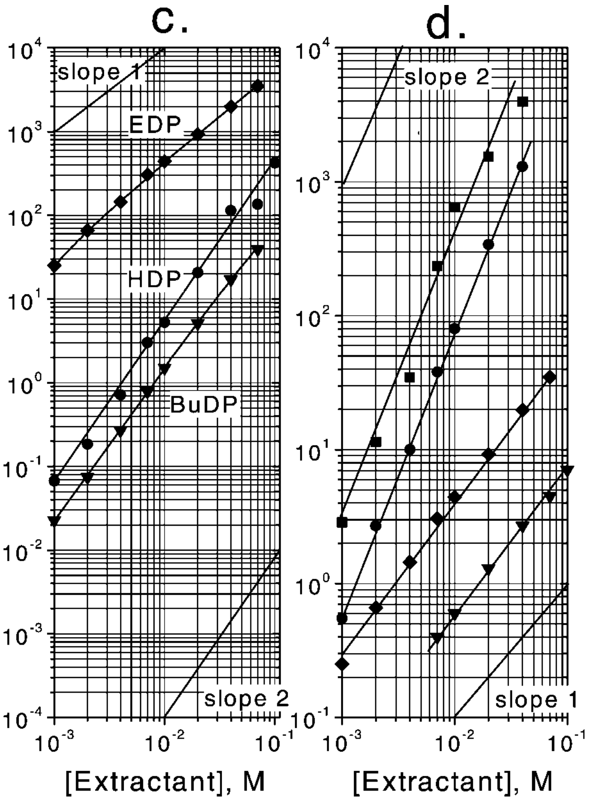


Figure 2. Continued.

lower concentrations and decrease slightly as the extractant concentration increases. This agrees with the vapor pressure osmometry data, which suggest that these ligands exist in toluene as an equilibrium mixture of trimeric and hexameric species and monomeric and hexameric species, respectively.[38] Thus, at lower extractant concentrations, Am(III) is extracted by two trimeric aggregates of H_2DTMSP[BuDP], while at higher extractant concentrations, extraction by a single hexameric aggregate becomes important. The extraction of Am(III) by H_2DTMSP[HDP] involves monomeric and hexameric species. VPO data indicate that H_2DTMSP[HDP] is somewhat less aggregated at a given extractant concentration than H_2DTMSP[EDP]. Speciation diagrams plotted using equilibrium aggregation constants calculated from the best fits of the VPO data for these ligands suggest that at a given extractant concentration, the concentration of monomeric H_2DTMSP[HDP] is much higher than that for H_2DTMSP[EDP].[37,38] Even at the highest extractant concentrations employed in the solvent extraction experiments, monomeric H_2DTMSP[HDP] composes a significant portion (∽ 25%) of the species present in solution. In the H_2DTMSP[EDP] system, this relative concentration of monomer is only observed at the lowest extractant concentrations (<0.002 M). A substantial deviation of the extractant dependency from slope 1 is also observed for H_2DTMSP[EDP] extraction of alkaline earth cations and Am(III) at low extractant concentration, which has been attributed to the contribution of the monomeric species to the metal ion extraction.

Additionally, since fitting of the vapor pressure osmometry data suggests that H_2DTMSP[HDP] tends to be more highly aggregated than H_2DTMSP[BuDP] at a given extractant concentration, the slightly more efficient extraction of Am(III) observed for H_2DTMSP[HDP] vs H_2DTMSP[BuDP] suggests that extraction by this single hexameric aggregate is more efficient than extraction by two trimeric species. Furthermore, extraction of Am(III) by H_2DTMSP[BuDP] and H_2DTMSP[HDP] is more efficient than extraction by the dimeric ligands H_2DTMSP[PrDP] or H_2DTMSP[PDP] 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 H_2DTMSP[MDP], where the chelate effect is the dominant factor in determining extraction efficiency.

The importance of aggregation in the determination of the efficiency of metal ion extraction by these ligands is clearly illustrated by the remarkably different behavior exhibited by these extractants in the depolymerizing diluent 1-decanol. Figure 3 shows data obtained for the extraction of Am(III) from 0.01-M HNO_3 by the series of silyl-substituted diphosphonic acids in 1-decanol as a function of the extractant concentration. In the absence of extractant aggregation, the efficiency of Am(III) extraction decreases as the number of bridging methylene groups is increased. As observed previously for the 2-ethylhexyl extractants,[49] a slope of 2 is observed at low extractant concentrations, consistent with extraction of each Am(III) cation by two molecules of extractant. At higher extractant concentrations, slopes closer to 3 are observed in the extractant dependency plots as the extracted species consists of Am(III) complexed to three extractant molecules. The more dramatic increase in the slope of the extractant dependency plot observed for Am(III) extraction by H_2DTMSP[HDP] suggests a tendency for this extractant to form more highly self-solvated species in which Am(III) is complexed by additional fully protonated extractant molecules. However, this phenomenon is being investigated further to rule out other possible explanations for this behavior, such as the extractant remaining aggregated to some extent in 1-decanol.

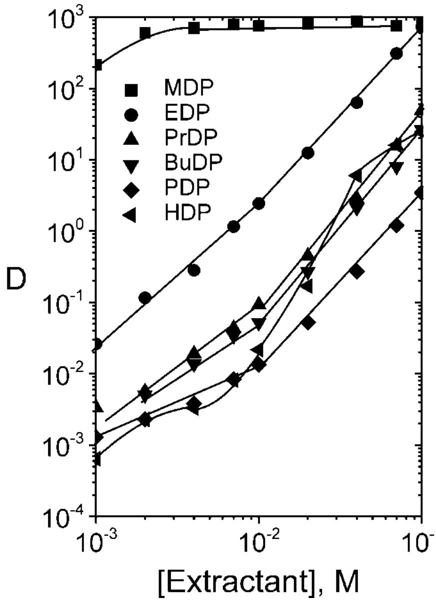


Figure 3. Extraction of Am(III) from 0.01-M HNO_3 by H_2DTMSP[MDP], H_2DTMSP[EDP], H_2DTMSP[PrDP], H_2DTMSP[BuDP], H_2DTMSP[PDP], and H_2DTMSP[HDP] in 1-decanol as a function of the extractant concentration in the organic phase.

Figure 2d shows the data for the extraction of Am(III) by H_2DEH[MDP], H_2DTMSP[MDP], H_2DEH[EDP], and H_2DTMSP[EDP] in *o*-xylene from 1.0-M HNO_3 as a function of extractant concentration. While the silyl-substituted extractants exhibit nearly identical aggregation behavior as their 2-ethylhexyl analogues, the silyl-substituted compounds tend to extract metal ions two to three times more efficiently. ^{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,[37,38] due to the increased electron-donating nature of the trimethylsilyl group. However, the effect of this electron-donating nature on the phosphoryl groups is expected to be minimal because the trimethylsilyl group is separated from the rest of the molecule by a three carbon chain. Nevertheless, small, but consistent, decreases in the energy of the infrared P═O stretching bands and increases in the ^{31}P NMR chemical shifts are observed for the silyl-substituted compounds relative to their 2-ethylhexyl substituted analogues. Differences between the solubility of the extracted complexes in the aqueous and organic phases may also explain the increased extraction efficiency of the silyl substituted extractants. Data for the distribution of the 2-ethylhexyl extractants between *o*-xylene and aqueous nitric acid as a function of extractant concentration has been reported.[50] However, the distribution ratios obtained are at the upper limit measurable by the ICP-AES method used to quantify the amount of extractant in the aqueous phase, so it is unlikely that any significant difference in aqueous phase solubility would be observed for the silyl-substituted compounds. Therefore, quantitative data on the solubility of the two series of extractants is not available. However, qualitative data obtained during the synthesis of the metal salts of H_2DTMSP[MDP][51] and H_2DEH[MDP][52] suggest that the metal complexes of H_2DTMSP[MDP] are much less water soluble than those of H_2DEH[MDP].

SCCO$_2$ Solubility

Figure 4a and b show the data obtained for dynamic flow experiments performed to determine the relative solubility of the silyl- and 2-ethylhexyl-substituted alkylenediphosphonic acids in unmodified SCCO$_2$ (at 250 bar, 60°C). As can be seen in the figure, the H_2DTMSP[MDP] is more soluble in SCCO$_2$ than H_2DEH[MDP], and the solubility of the two series of extractants varies dramatically with the length of the alkylene chain bridging the phosphorus atoms. The data from Fig. 3a and b was used to calculate the molar solubilities of the compounds in SCCO$_2$. These solubility values were obtained by dividing the amount of extractant recovered by the volume of $CO_2 +$ solute recovered.[53] In the case of H_2DTMSP[MDP], nearly all of the ligand used in the experiment was recovered from the first 3-mL sample collected. Therefore, the solubility of H_2DTMSP[MDP] was estimated using the first data point in Fig. 3a and b. The value reported in Table 2 is the average of three determinations. For the other extractants, a linear relationship is observed for the amount of solute recovered and the volume of CO_2 collected over at least part of the volume range reported. The solubility values reported in Table 2 for these compounds are the average value obtained over a much larger number of determinations.

The increased solubility observed for H_2DTMSP[MDP] over H_2DEH[MDP] was unexpected based on preliminary experiments performed with liquid CO_2. However, this is not inconsistent with data

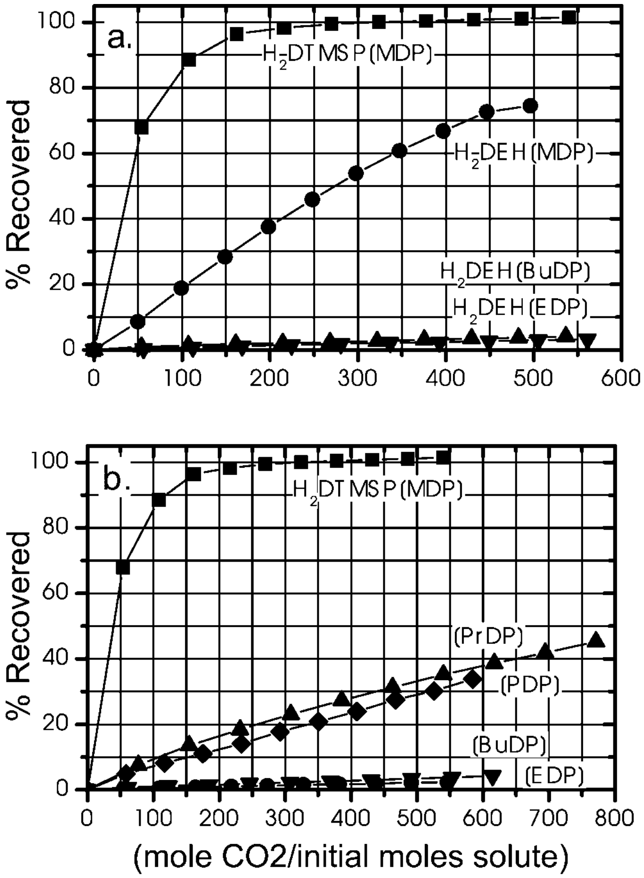


Figure 4. a. Percentage solute recovered vs moles CO_2 per initial moles of solute for H_2DTMSP[MDP], H_2DEH[MDP], H_2DEH[EDP], H_2DEH[BuDP]. Experiment performed at 60°C and 250 bar using unmodified CO_2. b. Percentage solute recovered vs moles CO_2 per initial moles of solute for H_2DTMSP[MDP], H_2DTMSP[EDP], H_2DTMSP[PrDP], H_2DTMSP[BuDP], and H_2DTMSP[PDP]. Experiment performed at 60°C and 250 bar using unmodified CO_2.

obtained for compounds containing siloxane functionalities, for which the $SCCO_2$ solubility is highly pressure dependent.[54] The data suggest that the incorporation of trimethylsilyl functionalities can significantly increase the $SCCO_2$ solubility of compounds. However, since the branching of

Table 2. Solubilities of alkylenediphosphonic acids in $SCCO_2$.[a]

	Trimethylsilyl-esterified compounds		2-Ethylhexyl-esterified compounds	
n[b]	M.W.[c]	Solubility[d]	M.W.[c]	Solubility[d]
1	404.51	2.0×10^{-1}	400.41	3.3×10^{-2}
2	418.53	8.4×10^{-4}	414.43	8.6×10^{-4}
3	432.56	1.7×10^{-2}	—	—
4	446.58	1.1×10^{-3}	442.48	1.2×10^{-3}
5	460.61	1.3×10^{-2}	—	—

[a] In all cases, solubilities reproducible within ± 5%.
[b] Number of bridging methylene groups.
[c] Molecular weight in g/mole.
[d] Solubility in $SCCO_2$ at 60°C and 250 bar in moles/L.

organic molecules has been shown to affect their solubility in $SCCO_2$,[55] the $SCCO_2$ solubility of partially esterified diphosphonic acids containing eight carbon alkylene chain functionalities with various degrees of branching are currently being studied to determine whether the observed solubility enhancement is due to the silyl functionality or to the increased branching relative to the 2-ethylhexyl functionality.

The second trend apparent in Fig. 4a and b, and more quantitatively described in Table 2, is the dramatic effect of alkylene bridge length on the $SCCO_2$ solubility of these compounds. Although no aggregation data are currently available for these compounds in $SCCO_2$, data obtained for acetic and palmitic acids in toluene and $SCCO_2$[39] suggest that similar aggregation behavior may be observed in these diluents. The carboxylic acids are primarily dimeric in toluene and $SCCO_2$, with dimerization constants five to six times lower in $SCCO_2$. Assuming that similar aggregation behavior is observed for partially esterified diphosphonic acids in these two diluents as well, the solubility data suggest that aggregation is an important factor in determining $SCCO_2$ solubility. The extractants that are dimeric in toluene are significantly more soluble than those that form more highly aggregated species. Experiments using alcohol-modified $SCCO_2$ are currently being performed in our laboratory to provide a better understanding of the role of aggregation in this phenomenon.

CONCLUSION

The aggregation, solvent extraction, and $SCCO_2$-solubility properties of a series of trimethylsilyl-substituted partially esterified alkylenediphosphonic acids was studied and compared to an analogous series of 2-ethylhexyl-substituted compounds. These properties were found to vary dramatically as the length of the alkylene bridge separating the phosphorus atoms was increased. The aggregation and solvent extraction behavior of the silyl-substituted compounds was found to closely mimic that of the analogous 2-ethylhexyl-substituted extractants, with the silyl-substituted extractants typically extracting metal ion two to three times more efficiently. The $SCCO_2$ solubility of H_2DTMSP[MDP] was found to be significantly higher than that of H_2DEH[MDP], suggesting that the incorporation of silyl functionalities could be a useful method for increasing the $SCCO_2$ solubility of compounds. Additionally, the extractants that form dimeric aggregates in toluene were found to be significantly more soluble in $SCCO_2$ than those that form more highly aggregated species in toluene.

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