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Metal extraction by silyl-substituted diphosphonic acids. II. Effect of alkylene bridge length on aggregation and metal ion extraction behavior

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METAL EXTRACTION BY SILYL-SUBSTITUTED DIPHOSPHONIC ACIDS. II. EFFECT OF ALKYLENE BRIDGE LENGTH ON AGGREGATION AND METAL ION EXTRACTION BEHAVIOR

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ABSTRACT

In an ongoing effort to determine the relationship between structure and function in diphosphonic acids, the aggregation and solvent extraction chemistry of four novel silicon-substituted diphosphonic acids, *P*,*P*′-di[3-(trimethylsilyl)-1-propyl] propylene- (H_2DTMSP[PrDP]), butylene- (H_2DTMSP[BuDP]), pentylene- (H_2DTMSP[PDP]), and hexylene diphosphonic acid (H_2DTMSP[HDP]), were investigated. Vapor pressure osmometry indicates that H_2DTMSP[PrDP] and H_2DTMSP[PDP] are dimeric in toluene at 25°C, while H_2DTMSP[BuDP] and H_2DTMSP[HDP] are primarily trimeric and hexameric, respectively. The solvent extraction of selected alkaline earth cations (Ca, Sr, and Ba) and representative tri-, tetra-, and hexavalent actinides

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[Am(III), Th(IV), and U(VI)], from nitric acid solutions into *o*-xylene solutions of the ligands has been studied and compared to results reported previously for some analogous di(2-ethylhexyl)-substituted diphosphonic acids. Differences observed in the magnitude of distribution ratios, based on the number of bridging methylene groups, have been explained considering factors such as ligand aggregation, chelate ring size, P=O basicity (qualitatively determined by ^{31}P nuclear magnetic resonance and infrared spectroscopy), and the relative acidities of the ligands.

Key Words: Diphosphonic acids; Silyl-substituted; Aggregation; Metal ion extraction

INTRODUCTION

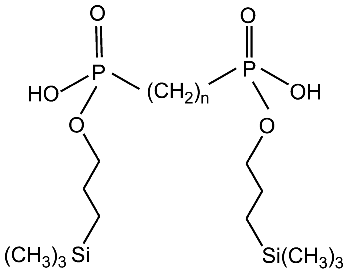
Diphosphonic acids have been investigated extensively as metal ion complexants (1–5). Numerous studies have demonstrated that these compounds form extraordinarily strong complexes with a variety of metal ions, even in strongly acidic media (5,6). In addition, upon appropriate substitution, these compounds have been shown to provide the basis for powerful metal ion extractants (6–8), a variety of novel ion-exchange (9–15), and extraction chromatographic (16) materials.

Over the past decade, supercritical carbon dioxide ($SCCO_2$) has received considerable interest as an environmentally benign alternative to conventional organic solvents. Additionally, $SCCO_2$ possesses a number of unique properties, such as low viscosity and high diffusivity, which make it a potentially useful diluent for solvent extraction (17). Therefore, coupling the high affinity of diphosphonic acids for metal ions and the unique properties of $SCCO_2$ could provide a powerful tool for many solvent extraction applications. Unfortunately, preliminary experiments have shown that neither the unsubstituted diphosphonic acids nor the partially esterified diphosphonic acids studied to date (i.e., 2-ethylhexyl alkylenediphosphonic acids) are sufficiently soluble in unmodified CO_2 to be useful solvent extraction reagents in this diluent (18).

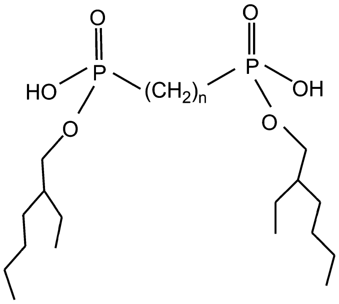
Siloxane polymers and fluorinated compounds have been shown to be quite soluble in $SCCO_2$ (19,20). In an effort to synthesize diphosphonic acid extractants that are more soluble in $SCCO_2$ than either the unsubstituted or 2-ethylhexyl-substituted diphosphonic acids, we have attempted to incorporate silicon and fluorine functionalities into diphosphonic acids (21). This manuscript details the aggregation and solvent extraction properties of a series of partially esterified alkylenediphosphonic acids containing the 3-(trimethylsilyl)-1-propyl functionality. 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 incorporated into diphosphonic acids using a well-characterized method (22). Furthermore, separating the trimethylsilyl functionality from the remainder of the molecule with a three-carbon chain provides optimal chemical stability and synthetic accessibility (23).

The incorporation of the silyl functionality was not expected to enhance the $SCCO_2$ solubility of diphosphonic acids significantly, and preliminary experiments performed with liquid CO_2 suggested that no solubility enhancement was achieved over alkyl-substituted diphosphonic acids (18). However, recent experiments performed using $SCCO_2$ (60°C, 250 bar) show a significant enhancement of the $SCCO_2$ solubility of silyl-substituted diphosphonic acids over their alkyl-substituted analogs (24). This is consistent with data obtained for compounds containing siloxane functionalities, for which the $SCCO_2$ solubility is highly pressure dependent (25), and suggests that incorporation of the trimethylsilyl functionality can increase the $SCCO_2$ solubility of compounds.

In an earlier study (26) undertaken as a first step in evaluating the potential utility of silyl-substituted diphosphonic acids as metal ion extractants in $SCCO_2$, we examined the extraction of selected alkaline earth and actinide cations into *o*-xylene by *P*,*P*′-di[3-(trimethylsilyl)-1-propyl] methylenediphosphonic acid (H_2DTMSP[MDP]) and its ethylene homologue, *P*,*P*′-di[3-(trimethylsilyl)-1-propyl] ethylenediphosphonic acid (H_2DTMSP[EDP]) (Structure I, with $n = 1$ and 2, respectively). The aggregation and solvent extraction behavior of these ligands was found to closely parallel that of the corresponding *P*,*P*′-di(2-ethylhexyl) alkylenediphosphonic acids (Structure II), indicating that incorporation of the silyl functionality has no adverse impact on the metal ion extraction properties of these compounds. More striking was the profound effect on the aggregation and solvent extraction properties of these silyl-substituted compounds observed upon varying the length of the alkylene



Structure I.



Structure II.

bridge separating the phosphoryl groups. For example, while H_2DTMSP[MDP] is dimeric in toluene, H_2DTMSP[EDP] is primarily hexameric. Similarly, while H_2DTMSP[MDP] exhibits virtually no extraction selectivity amongst the alkaline earth cations, H_2DTMSP[EDP] preferentially extracts calcium over strontium, barium, and radium, much like a monofunctional organophosphorus extractant. While more selective, however, H_2DTMSP[EDP] typically extracts alkaline earth cations 10–100 times less efficiently than H_2DTMSP[MDP] (26).

A number of factors, including P=O basicity, P—OH acidity, chelate ring size, and aggregation, must be considered in order to explain the dramatically different solvent extraction behavior observed for H_2DTMSP[MDP] and H_2DTMSP[EDP]. In an effort to determine the relationship of these various factors in the extraction of metal cations by diphosphonic acids, we have measured the extraction of selected alkaline earth and representative tri-, tetra-, and hexavalent actinide cations, from nitric acid, into *o*-xylene by four additional silyl-substituted diphosphonic acids, *P*,*P*′-di[3-(trimethylsilyl)-1-propyl] propylene-, butylene-, pentylene-, and hexylene- diphosphonic acid (H_2DTMSP[PrDP], H_2DTMSP[BuDP], H_2DTMSP[PDP], and H_2DTMSP[HDP], i.e. Structure I, with $n = 3-6$, respectively. These results have been compared to those described previously for H_2DTMSP[MDP], H_2DTMSP[EDP], and (where such results are available) for the conventional di(2-ethylhexyl)-substituted alkylenediphosphonic acids (Structure II).

Additionally, we have examined the aggregation behavior of these compounds, an understanding of which is essential for proper interpretation of the extraction data. Furthermore, given recent reports of differences in the $SCCO_2$ solubility of the monomeric and dimeric forms of various carboxylic acids (27,28), 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

H_2DTMSP[MDP], H_2DTMSP[EDP], H_2DTMSP[PrDP], and H_2DTMSP[BuDP] were synthesized and characterized as described previously (22) through the dicyclohexylcarbodiimide facilitated coupling of one molar equivalent of the appropriate alkylenediphosphonic acid with two molar equivalents of 3-trimethylsilyl-1-propanol in tetrahydrofuran. The ligands were shown to be greater than 97% pure by potentiometric titration with standard base (J. T. Baker Chemical Co. Phillipsburg, N.J.). Aqueous solutions were prepared using water from a Milli-Q2 purification system and Ultrex Reagent nitric acid (J. T. Baker Chemical Co. Phillipsburg, N.J.). Organic solutions used in solvent extraction experiments were prepared by dissolving a known mass of the extractant in enough *o*-xylene (Aldrich Chemical Co. Milwaukee, WI) to achieve the desired molarity. The radionuclides ^{45}Ca, ^{85}Sr, and ^{133}Ba were obtained from Isotospe Product Laboratories (Burbank, CA). ^{241}Am, ^{233}U, and ^{230}Th were obtained from ANL (Argonne National Laboratory, Argonne, IL) stocks. Only freshly purified ^{233}U and ^{230}Th were used in the extraction experiments. Radionuclides were used at tracer level concentration. Sodium salts of the extractants were synthesized as described previously (29) by neutralizing solutions of the extractants in methanol with two equivalents of standard NaOH. The novel compounds H_2DTMSP[PDP] and H_2DTMSP[HDP] were synthesized and purified by the method described previously (22).

P,*P*′-di[3-(trimethylsilyl)-1-propyl] pentylenediphosphonic acid, H_2DTMSP[PDP]. Equivalent Wt.: calcd 230 g mol^{-1}, obs. 233 g mol^{-1}. ^{31}P NMR ($CDCl_3$) singlet at δ 34.74 ppm. ^{1}H NMR ($CDCl_3$) δ 0.01 (s, 18H, $Si(CH_3)_3$), 0.49 (m, 4H, $OCH_2CH_2C\mathit{H}_2$), 1.50 (m, 2H, $PCH_2CH_2C\mathit{H}_2CH_2CH_2P$), 1.66 (br, m, 12H, $OCH_2C\mathit{H}_2$, $PC\mathit{H}_2C\mathit{H}_2CH_2C\mathit{H}_2C\mathit{H}_2P$), 3.97 (dt, 4H, $J_{P,H} = J = 7.1$ Hz, OCH_2), 10.11 (s, 2H, OH) ppm. Obtained as a clear oil in 60% yield.

P,*P*′-di[3-(trimethylsilyl)-1-propyl] hexylenediphosphonic acid, H_2DTMSP[HDP]. Equivalent Wt.: calcd 237 g mol^{-1}, obs. 235 g mol^{-1}. ^{31}P NMR ($CDCl_3$) singlet at δ 34.38 ppm. ^{1}H NMR ($CDCl_3$) $\delta - 0.01$ [s, 18H, $Si(CH_3)_3$], 0.48 (m, 4H, $OCH_2CH_2C\mathit{H}_2$), 1.45 (m, 4H, $PCH_2CH_2C\mathit{H}_2C\mathit{H}_2CH_2CH_2P$), 1.65 (br, m, 12H, $OCH_2C\mathit{H}_2$, $PC\mathit{H}_2C\mathit{H}_2CH_2C\mathit{H}_2C\mathit{H}_2P$), 3.97 (dt, 4H, $J_{P,H} = J = 7.1$ Hz, OCH_2), 10.11 (s, 2H, OH) ppm. Obtained as a clear oil in 58% yield.

Measurements

Vapor pressure osmometric (VPO) and distribution ratio measurements were made using the same techniques, instrumentation, and procedures described previously (6,30). 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 at room temperature (22 ± 1°C). Typically, a solution of the extractant in *o*-xylene was preequilibrated with an equal volume of an aqueous nitric acid solution. Then, a 500 μL aliquot of the preequilibrated organic phase was vortexed with an equal volume of an identical aqueous phase spiked with 3–5 μL of radiotracer dissolved in aqueous HNO_3. Preliminary experiments showed that 5 min 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 Auto Gamma (^{90}Sr, ^{133}Ba, and ^{241}Am) counter or Packard 2200CA (Packard Instrument Co. Meriden, CT) liquid scintillation counter (^{45}Ca, ^{223}Ra, ^{230}Th, and ^{233}U). 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 $D < 10^{-3}$).

The VPO measurements were performed on a Jupiter Model 833 (Jupiter Instrument Co., Jupiter, FL) vapor pressure osmometer thermostated to 25.0 ± 0.1°C by a Neslab constant temperature bath. The instrument was calibrated using standard toluene solutions of sucrose octaacetate. A plot of measured voltage versus sucrose octaacetate molality (m) gave a slope of 1788 $\mu V\,m^{-1}$ for the instrument calibration constant. Toluene, due to its lower boiling point, is a more convenient diluent than *o*-xylene for the VPO measurements. However, the extractant aggregation is expected to be the same in toluene and *o*-xylene.

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 and their sodium salts were recorded in $CDCl_3$ and D_2O (Aldrich Chemical Co.), respectively, by collecting 100 scans on a Varian 400 MHz spectrometer. Chemical shifts are reported relative to an external 85% H_3PO_4 reference.

RESULTS AND DISCUSSION

Aggregation

H_2DTMSP[MDP] and H_2DTMSP[EDP] have been shown by VPO to be dimeric and primarily hexameric, respectively, in toluene at 25°C (26). Figure 1 compares the VPO data in toluene at 25°C for H_2DTMSP[PrDP], H_2DTMSP[BuDP], H_2DTMSP[PDP], and H_2DTMSP[HDP] with that of the monomeric standard sucrose octaacetate. These data indicate that H_2-

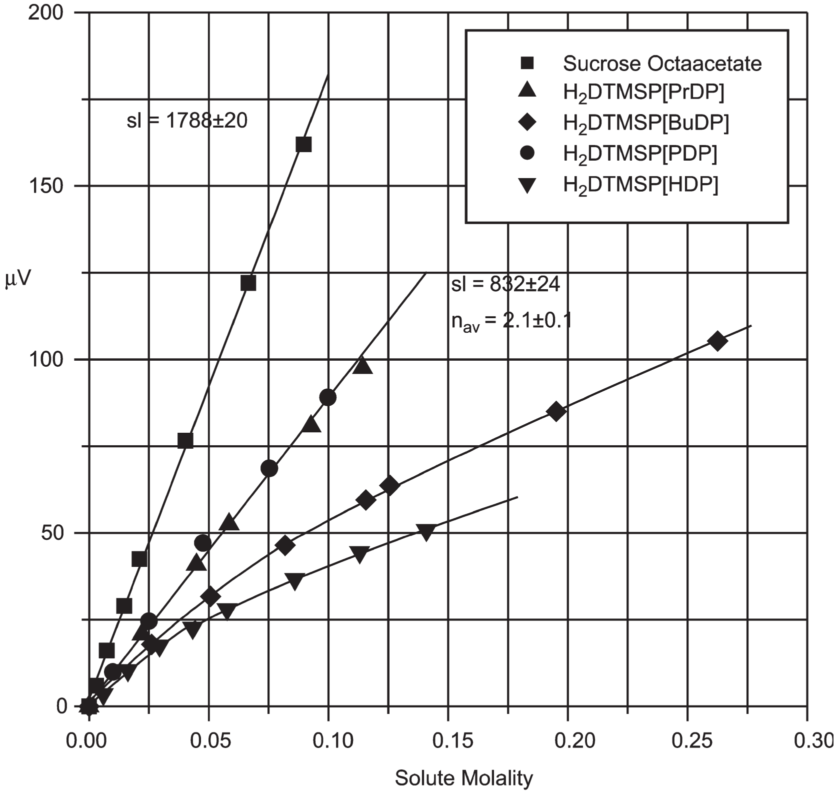


Figure 1. Vapor pressure osmometry measurements (microvolts, μV, vs. molality, m) for H_2DTMSP[PrDP], H_2DTMSP[BuDP], H_2DTMSP[PDP], H_2DTMSP[HDP] and the monomeric standard sucrose octaacetate in toluene at 25°C.

DTMSP[PrDP] and H_2DTMSP[PDP] are dimeric in toluene at 25°C. The linearity of the H_2DTMSP[PrDP] and H_2DTMSP[PDP] VPO data indicates that the aggregation constants for these ligands are sufficiently large that the aggregation of the extractants remains unchanged over the concentration range studied.

In contrast, the data for H_2DTMSP[BuDP] and H_2DTMSP[HDP] are not linear, indicating an equilibrium between two or more species of different aggregation number. To develop a quantitative description of the equilibria involved in the aggregation of H_2DTMSP[BuDP] and H_2DTMSP[HDP], the VPO data was plotted as the average aggregation number (n_{ave}) vs. the solute molality (Figs. 2a and 3a). The average aggregation

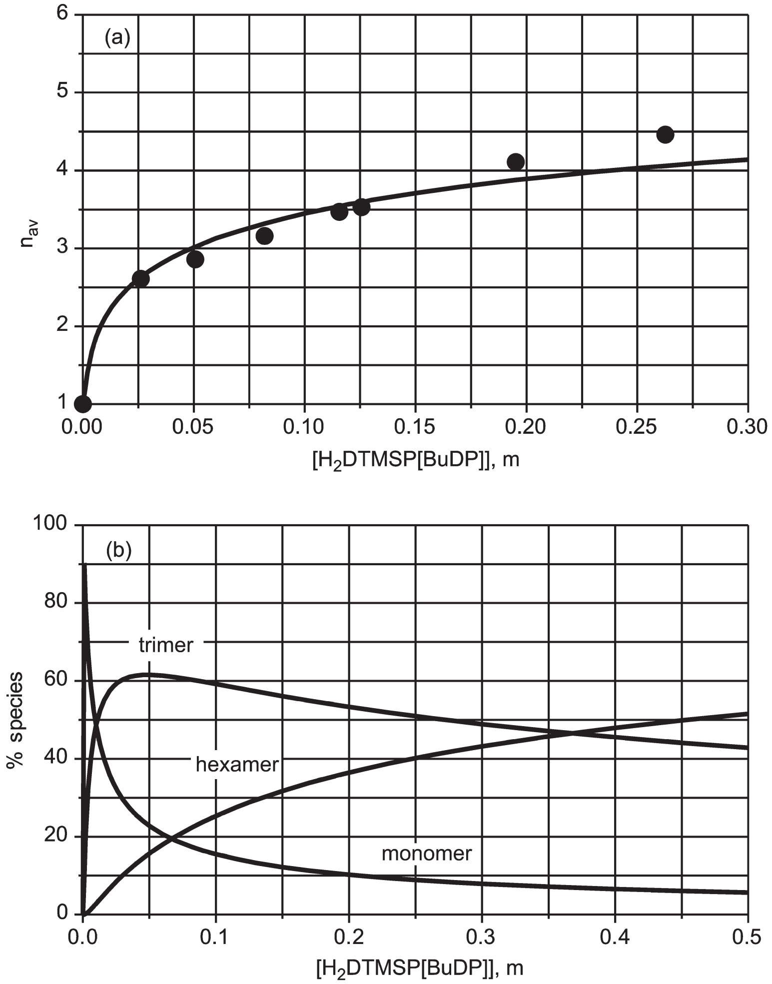


Figure 2. (a) Average aggregation number (n_{av}) vs. molality (m), for $H_2DTMSP[BuDP]$. (Solid line is calculated employing the values of β_3 and β_6 reported in the text.) (b) Distribution of $H_2DTMSP[BuDP]$ between monomeric, trimeric, and hexameric species as a function of total solute concentration.

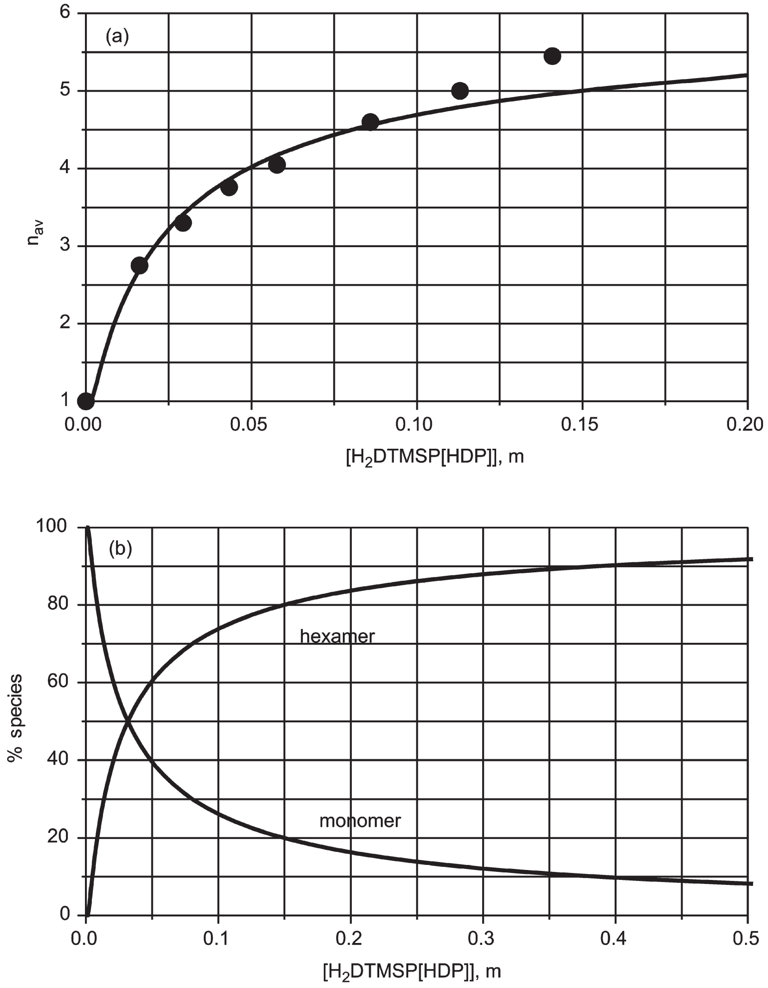


Figure 3. (a) Average aggregation number (n_{av}) vs. molality (m), for H_2DTMSP[HDP]. (Solid line is calculated employing the value of β_6 reported in the text.) (b) Distribution of H_2DTMSP[HDP] between monomeric and hexameric species as a function of total solute concentration.

number is defined as

$$n_{\text{ave}} = C_{\text{tot}}/S \tag{1}$$

$$S = \mu V/K_{\text{r}} \tag{2}$$

where C_{tot} is the analytical concentration of H_2DTMSP[BuDP] or H_2DTMSP[HDP], S the sum of the concentrations of each species present, μV the instrument reading, and K_{r} the slope of the sucrose octaacetate reference line. By fitting this data using the procedure and methods described in Ref. (8), the equilibrium aggregation constants (β_n, where n is the aggregation number) were calculated for a number of possible combinations of equilibria. The results of these calculations indicate that the model that best describes the aggregation of H_2DTMSP[BuDP] involves the formation of trimeric and hexameric species, with $\beta_3 = (1.9 \pm 0.5) \times 10^5$ and $\beta_6 = (9.0 \pm 1.3) \times 10^{11}$. The model that best describes the aggregation of H_2DTMSP[HDP] involves the formation of hexameric species, with $\beta_6 = (5.2 \pm 1.3) \times 10^{11}$. A comparison of the experimental data with curves calculated using these equilibrium aggregation constants is shown in Figs. 2a and 3a.

Figures 2b and 3b show the species distribution diagrams calculated using the equilibrium aggregation constant values reported earlier. From these plots, it is evident that while the H_2DTMSP[BuDP] trimer is the predominant species in the concentration range over which the extraction experiments were run, the concentrations of the hexamer and the monomer are not negligible. The species distribution diagram for H_2DTMSP[HDP] is similar to that for H_2DTMSP[EDP] (26). However, H_2DTMSP[HDP] is slightly less aggregated at a given concentration of extractant, consistent with its β_6, which is a factor of two lower than that for H_2DTMSP[EDP]. Since the aggregation of an extractant can profoundly affect its extraction properties, the presence of these various species must be taken into account to fully explain the H_2DTMSP[BuDP] and H_2DTMSP[HDP] solvent extraction data.

Consideration of the aggregation for all six of the substituted diphosphonic acid ligands reveals the presence of an even–odd effect as the number of methylene groups bridging the phosphorus atoms is varied. The ligands with an odd number of methylene linkers form dimeric aggregates in toluene, whereas those with an even number of methylene linkers form more highly aggregated species. While the origin of this effect is not yet fully understood, 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 POH groups of the ligands and changes the geometry of the hydrogen bonded aggregates that can be formed between the ligand molecules. As observed with normal "straight-chain" alkanes, this even–odd effect also manifests itself in the melting points of the partially esterified diphosphonic acids (22) and their unsubstituted analogs (31), with the ligands containing an even number of bridging methylene groups exhibiting melting points that are higher than expected. Molecular mechanics calculations are currently being performed to determine the most energetically stable conformations of these ligand aggregates.

^{31}P NMR and Infrared Spectroscopy

Tables 1 and 2 list the positions of the ^{31}P NMR chemical shifts and the phosphoryl infrared stretching bands, respectively, for a number of diphosphonates. As can be seen, the same general trends previously observed for the unsubstituted diphosphonic acids and their tetraethyl esters (31) hold for the silyl-substituted diphosphonic acids and their di(2-ethylhexyl) analogs. Specifically, the ^{31}P chemical shifts observed for the substituted diphosphonic acids become more positive as the number of methylene groups bridging the phosphorus atoms increases. The chemical shifts observed are analogous to those for monophosphonates in which the second phosphonate group present in the corresponding diphosphonate has been replaced by a highly electronegative substituent such as chlorine, i.e., $Cl(CH_2)_nP(O)(OR)(OH)$ (31).

As noted previously (32,33), the basicity of the P=O group and the acidity of the POH proton vary in opposite directions with the electronegativity of the substituents on the phosphorus atom. In the case of diphosphonic acids, as the number of bridging methylene groups increases, the basicity of the phosphoryl oxygens increase and the acidity of the POH protons decrease. On the basis of the position of the ^{31}P NMR chemical shifts observed for a series of unsubstituted diphosphonic acids, this trend continues until four methylene groups separate the phosphorus atoms (31). After this point, the incorporation of additional methylene groups has no effect on the ^{31}P chemical shift, and the observed chemical shift is equivalent to that of a monophosphonate with an alkyl substituent, i.e., $CH_3(CH_2)_nP(O)(OR)(OH)$.

On the basis of these considerations, the basicity of the phosphoryl groups is expected to follow the order $[MDP] \ll [EDP] < [PrDP] < [BuDP] \approx [PDP] \approx [HDP]$, with the acidities of the POH protons following the opposite order. The largest differences in phosphoryl basicity and POH proton acidity should be observed between [MDP] and [EDP], since the corresponding difference in chemical shift is the largest in this case. A more quantitative description of this effect is not possible since the compounds are not soluble in water. However, the pK_a values of an analogous series of water soluble partially esterified diphosphonic acids are currently being determined and may ultimately prove useful in the interpretation of these results. Additionally, the ^{31}P chemical

Table 1. ^{31}P Chemical Shifts for Diphosphonates (ppm vs. 85% H_3PO_4)

Compound $(YO)_2OP(CH_2)_nPO(OY)_2$	Tetra Acid[a]	Di(2-ethylhexyl) Ester[b]	Di[3-(trimetylsilyl)-1-propyl] Ester[b]	Disodium Salt of DTMSP Ester[c]
$n = 1$	16.7	19.9	20.0	17.5
$n = 2$	27.4	31.1	31.4	26.8
$n = 3$	28.2	N/A	33.5	27.5
$n = 4$	31.6	34.1	34.4	28.5
$n = 5$	31.9	N/A	34.7	29.1
$n = 6$	30.6	N/A	34.4	29.3
$n = 10$	28.6	N/A	N/A	N/A

[a] From Ref. 31.

[b] In $CDCl_3$.

[c] In D_2O.

Table 2. P=O Infrared Stretching Frequencies for Selected Diphosphonates (cm^{-1})

Compound $(YO)_2OP(CH_2)_nPO(OY)_2$	Tetraethyl Ester[a]	Di(2-ethylhexyl) Ester[b]	Di[3-(trimetylsilyl)-1-propyl] Ester[c]
$n = 1$	1266	1238	1230.0
$n = 2$	1261	1214	1212
$n = 3$	1250	N/A	1197
$n = 4$	1250	1200	1194
$n = 5$	1253	N/A	1192
$n = 6$	1252	N/A	1192
$n = 10$	1253	N/A	N/A

[a] From Ref. 31.
[b] From Ref. 35.
[c] In CCl_4 or toluene.

shifts of the silyl-substituted diphosphonic acids are slightly larger than in the analogous di(2-ethylhexyl) diphosphonic acids, suggesting that the P=O groups of the silyl-substituted ligands are slightly more basic. This difference may be due to the slightly higher electron-donating nature of the trimethylsilyl group relative to the 2-ethylhexyl group. This effect is expected to be small since the trimethylsilyl group is separated from the rest of the molecule by a three-carbon chain. However, experiments performed to determine the amount of nitric acid extracted by solutions of tetraesters of methylenediphosphonic acid suggest that P=O basicity increases with the incorporation of 3-trimethylsilyl-1-propyl esterifying groups, in spite of the relatively large separation of the trimethylsilyl functionality from the phosphoryl group (34).

Examination of the infrared spectra of the various diphosphonates leads to similar conclusions. As shown, the P=O stretching bands for the disubstituted diphosphonic acids (Table 2) are generally 30–50 cm^{-1} lower than for the analogous tetraethyl diphosphonates due to aggregation of the disubstituted acids through the formation of strong hydrogen bonds between the phosphoryl oxygens and the acidic protons of the partial esters. In both cases, however, the P=O stretching bands shift to lower energy as the number of bridging methylene groups increases. Because of possible complications due to the formation of hydrogen bonds, the shift observed for the disubstituted diphosphonic acids cannot be attributed solely to the change in basicity of the P=O oxygen. However, since the tetraethyl diphosphonates do not form hydrogen-bonded aggregates, the shift of the P=O bands in this case is solely dependent upon the electronic effects of the substituents and, therefore, is indicative of the increasing basicity of the P=O oxygen as the number of bridging methylene groups increases. Furthermore, in agreement with the ^{31}P NMR data, the appearance of the phosphoryl stretching bands of the silyl-substituted diphosphonic acids at lower energy than in the analogous di(2-ethylhexyl) compounds suggests that the phosphoryl oxygens of the silyl-substituted diphosphonic acids are somewhat more basic.

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 (6–8,26), infrared spectroscopy (30), VPO (30), and small angle neutron scattering data (36,37) suggest that 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 manuscript. In these extracted complexes, the individual diphosphonic acid molecules are either mono-deprotonated or fully protonated. Data for pK_a values of analogous series of unsubstituted diphosphonic acids (38) and dicarboxylic acids (39) 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

Alkaline Earth Metal Cations

Figures 4 and 5 show the acid dependency data at 0.1 *M* extractant and the extractant dependency data at 0.05 *M* HNO_3, respectively, for the extraction of selected alkaline earth cations with H_2DTMSP[PrDP], H_2DTMSP[BuDP], H_2DTMSP[PDP], and H_2DTMSP[HDP] in *o*-xylene. In all cases, extractant concentrations refer to the total analytical concentration of the extractant in the organic phase. The acid dependencies for all of the extractants exhibit slopes of -2, indicating the displacement of two protons from the ligand species upon extraction of the divalent metal cation into the organic phase.

The extraction behavior of H_2DTMSP[MDP] and H_2DTMSP[EDP] have been discussed in detail previously (26). A brief summary is necessary here, however, to emphasize the effect of the number of bridging methylene groups on the solvent-extraction behavior of these ligands. The acid dependency plots for the extraction of alkaline earth cations by all six ligands exhibit a slope of -2, suggesting the displacement of two acidic protons upon metal ion complexation. The slope of two exhibited by the extractant dependencies measured for the extraction of selected alkaline earth cations by H_2DTMSP[MDP] in *o*-xylene suggest extraction via equilibrium (3):

$$M^{2+} + 2\overline{(H_2Y)_2} \leftrightarrow \overline{M(HY{\cdot}H_2Y)_2} + 2H^+ \tag{3}$$

where bars indicate organic phase species, H_2Y represents the fully protonated extractant, and two protons are displaced as required by the acid dependency

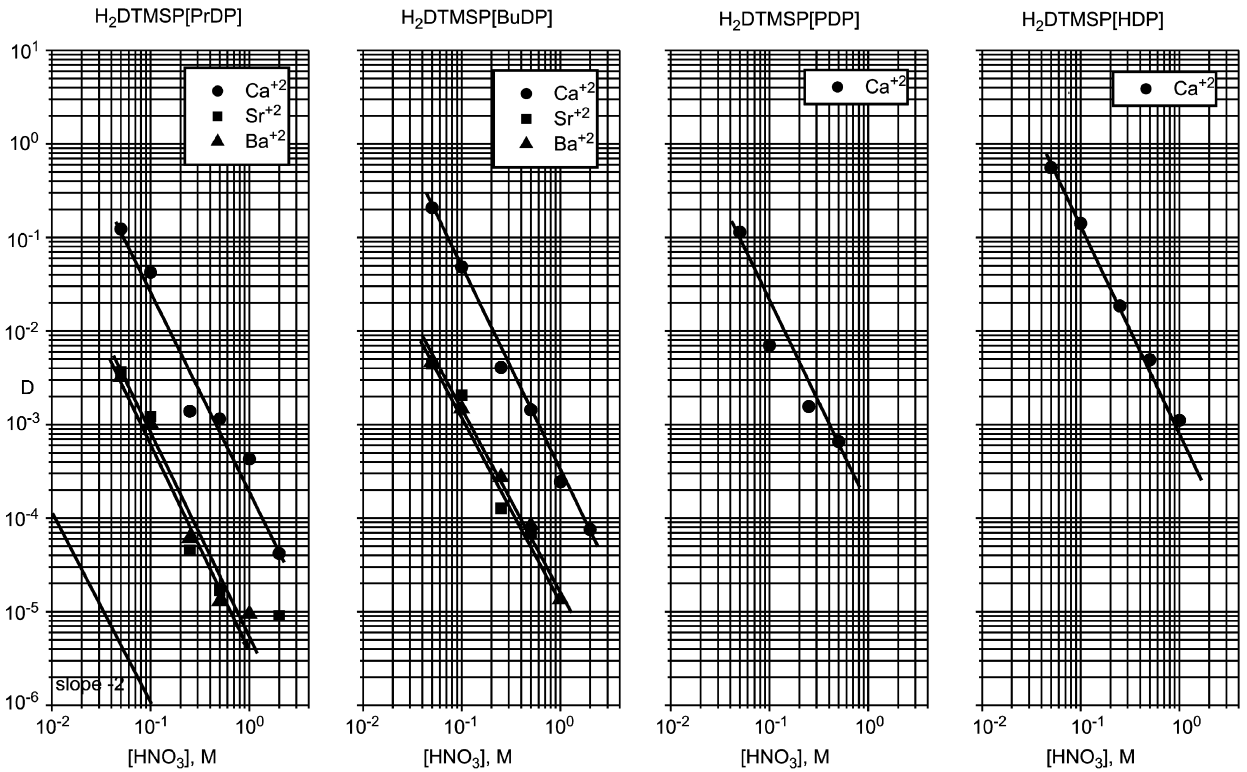


Figure 4. Acid dependencies at 25°C for the extraction of selected alkaline earth cations by 0.1 *M* H_2DTMSP[PrDP], H_2DTMSP[BuDP], H_2DTMSP[PDP], and H_2DTMSP[HDP] in *o*-xylene.

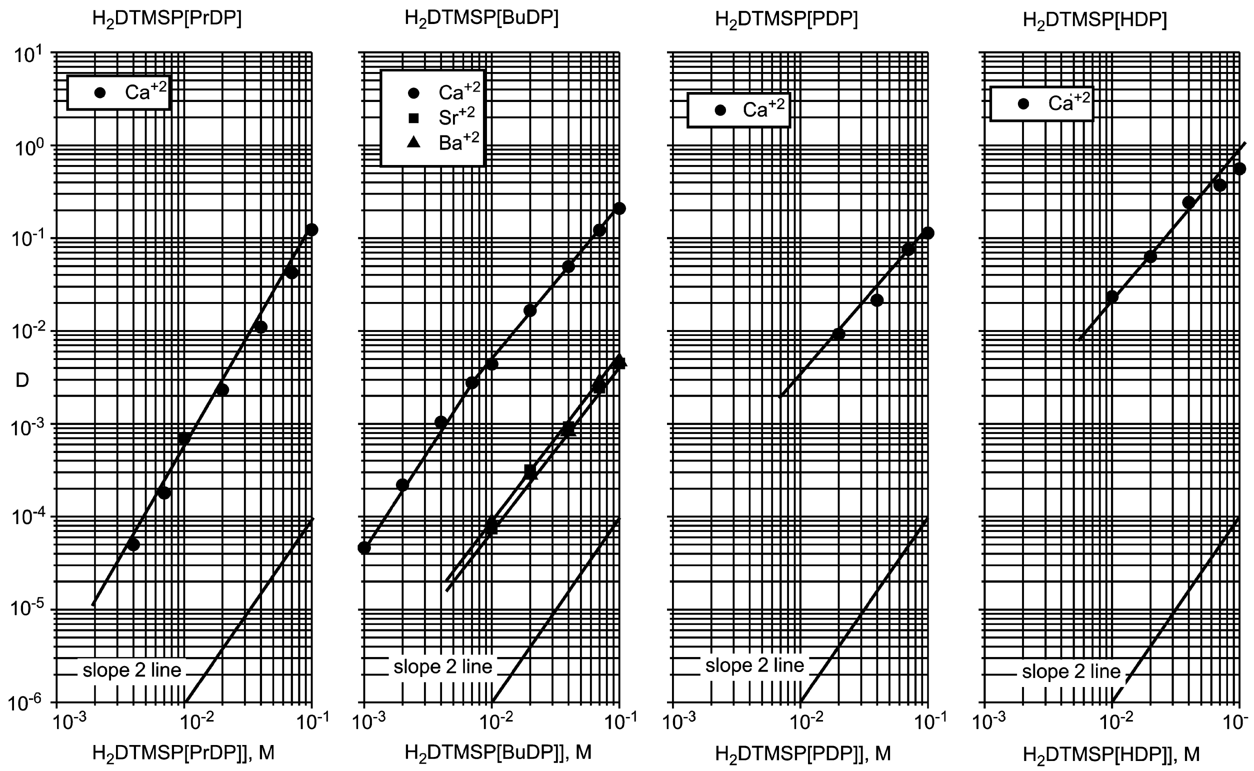


Figure 5. Extractant dependencies at 25°C for the extraction of selected alkaline earth cations by $H_2DTMSP[PrDP]$, $H_2DTMSP[BuDP]$, $H_2DTMSP[PDP]$, and $H_2DTMSP[HDP]$ in *o*-xylene from 0.05 *M* HNO_3.

slope of minus two. On the basis of this extraction equilibrium, a structure has been proposed for the alkaline earth–H_2DTMSP[MDP] complexes extracted into the organic phase, containing a number of six-membered chelate rings formed through the interaction of the phosphoryl oxygens of two mono-deprotonated H_2DTMSP[MDP] dimers with a single alkaline earth cation (6,26).

Alkaline earth cation extraction by H_2DTMSP[EDP] in *o*-xylene yields extractant dependencies of slope one. On the basis of this data, an equilibrium involving a doubly deprotonated hexameric aggregate has been proposed for the extraction of alkaline earth cations by H_2DTMSP[EDP] (7,26). In this structure, an alkaline earth metal cation lies in a hydrophilic cavity formed by the H_2DTMSP[EDP] aggregate, which resembles a reverse micelle. A number of seven- and eight-membered chelate rings are formed in this structure, and some of the coordination sites of the metal cation may be occupied by water molecules.

The extractant dependency data for the extraction of Ca by H_2-DTMSP[PrDP] and H_2DTMSP[PDP] exhibit slopes of 2.0 and 1.7, respectively. The deviation of the Ca-H_2DTMSP[PDP] extractant dependency data from slope two may be due to the solubility of the calcium complex in the aqueous phase, as suggested for H_2DEH[MDP] and H_2DTMSP[MDP] (6,26). Attempts to measure the extractant dependencies for Sr and Ba extraction by these ligands yielded *D* values below detection limits achievable employing reasonable amounts of radiotracer. However, it is reasonable to assume that Sr and Ba would exhibit similar behavior. Since H_2DTMSP[PrDP] and H_2DTMSP[PDP] have been shown by VPO to be dimeric in toluene, the slope of two suggests that each Ca cation is extracted by two dimeric aggregates of these ligands. As in the case of H_2DTMSP[MDP], the stoichiometry of alkaline earth extraction by H_2-DTMSP[PrDP] and H_2DTMSP[PDP] can be expressed by equilibrium (3).

The extractant dependency observed for Ca extraction by H_2-DTMSP[BuDP] exhibits a variable slope. At low extractant concentrations, the slope is close to 2, while at higher extractant concentrations, the slope is closer to 1.5. Together with the aggregation data obtained by VPO, this behavior suggests extraction of species of several different stoichiometries, which can be described by the following equilibria:

$$M^{2+} + \overline{H_2Y} \leftrightarrow \overline{MY} + 2H^+ \tag{4}$$

$$M^{2+} + 2(\overline{H_2Y})_3 \leftrightarrow \overline{M(H_5Y_3)_2} + 2H^+ \tag{5}$$

$$M^{2+} + (\overline{H_2Y})_6 \leftrightarrow \overline{MH_{10}Y_6} + 2H^+. \tag{6}$$

As can be seen by the species distribution (Figure 2b), at low extractant concentrations, the monomeric and trimeric H_2DTMSP[BuDP] species predominate, suggesting that extraction should occur primarily via equilibria (4) and (5). Studies of metal cation extraction by H_2DEH[BuDP] in 1-decanol (a monomerizing diluent) (40) have shown that alkaline earth cations are readily extracted by monomeric H_2DEH[BuDP]. The deviation from the slope two expected from extraction via equilibrium (5), which involves complexation of a given metal ion by two H_2DTMSP[BuDP] trimers, can be attributed to a contribution to the extraction of alkaline earth cations by equilibrium (4). The lower slope observed at higher extractant concentrations can be attributed to the increasing importance of equilibrium (6) to the overall extraction of alkaline earth cations. Extraction via complexes of this stoichiometry would yield extractant dependencies of slope one, as those observed for alkaline earth cation extraction by H_2DTMSP[EDP] in *o*-xylene.

Extraction of Ca by H_2DTMSP[HDP] in *o*-xylene yields an extractant dependency exhibiting a slope of 1.6. This indicates that extraction does not occur primarily via complexation of Ca to a single hexameric aggregate, as observed with H_2DTMSP[EDP] (26). This may be due to the increased importance of monomeric H_2DTMSP[HDP] suggested by the VPO data. This phenomenon will be discussed more thoroughly for the Am(III) extractant dependency data, which cover a wider range of extractant concentrations (vide infra).

The data in Figs. 4 and 5 and data previously published for the extraction of alkaline earth metal cations by H_2DTMSP[MDP] and H_2DTMSP[EDP] (26) indicate that the efficiency of metal ion extraction by these silyl-substituted diphosphonic acids follows the series [MDP] > [EDP] > [HDP] > [BuDP] > [PrDP] > [PDP]. The order of this series does not correspond to the expected trends in P=O basicity, POH acidity, or the size of chelate rings possible upon metal ion complexation. This suggests that these factors, as well as the aggregation state of the ligand, have varying degrees of importance as the number of methylene groups bridging the phosphorus atoms of these extractants is increased. This will be explained in more detail in the discussion of the Am(III) extraction data, which depict the trends in metal ion extraction more clearly.

Another trend that is evident from the data in Figs. 4 and 5 and data previously obtained for the extraction of alkaline earth metal cations by di(2-ethylhexyl)-substituted diphosphonic acids (6–8) is that the extraction of alkaline earth cations by the silyl-substituted diphosphonic acids is more efficient than by their di(2-ethylhexyl) analogs. This difference may be due to the somewhat higher basicities of the P=O oxygens (lower acidities of the P–OH groups) in the silyl derivatives (suggested by NMR and IR data) and/or differences in the solubility of the metal complexes of silyl derivatives in the aqueous and organic phases (suggested by qualitative observations in the synthesis of metal complexes for IR and magnetic susceptibility determinations (29,41)).

Am(III) Extraction

Figure 6 shows the nitric acid dependency and extractant dependency data for the extraction of Am(III) by solutions of H_2DTMSP[MDP], H_2DTMSP[EDP], H_2DTMSP[PrDP], H_2DTMSP[BuDP], H_2DTMSP[PDP], and H_2DTMSP[HDP] in *o*-xylene. The data for H_2DTMSP[MDP] and H_2DTMSP[EDP] have been previously discussed in detail (26), but are summarized here to illustrate the impact of varying the number of bridging methylene groups on the extraction properties of this series of ligands.

The acid dependency data for the extraction of Am(III) by the entire series of ligands exhibit slopes of close to -3 over at least a part of the HNO_3 concentration range studied, consistent with the displacement of three protons upon the extraction of a trivalent metal ion. However, at higher HNO_3 concentrations ($>0.5\,M$), the slope of the H_2DTMSP[PrDP] and H_2DTMSP[HDP] acid dependency approaches 0, while the slopes of the H_2DTMSP[PDP] and H_2DTMSP[BuDP] acid dependencies become positive. This behavior is consistent with extraction by fully protonated neutral extractants via a solvating mechanism, where extraction into the organic phase is dependent on the coextraction of nitrate ions for charge neutralization. This provides additional evidence that the ligands become less acidic as more methylene groups separate the phosphorus atoms. As more bridging methylene groups are incorporated, the POH protons of the ligands become less acidic and extraction via the solvating mechanism becomes more important at high aqueous acidities. The acidities at which the solvation mechanism manifests itself are generally lower for the ligands with more basic P=O groups.

Figure 6b and c show the extractant dependency data for the extraction of Am(III) by the dimeric and more highly aggregated ligands, respectively. The extractant dependencies of slope two observed for extraction of Am(III) by H_2DTMSP[MDP], H_2DTMSP[PrDP], and H_2DTMSP[PDP] (Fig. 6b) are consistent with the extraction of Am(III) cations by two dimeric aggregates. An extractant dependency of slope one is observed for Am(III) extraction by H_2DTMSP[EDP] (Fig. 6c), suggesting extraction by a single hexameric aggregate. In contrast, extractant dependencies for Am(III) extraction by H_2DTMSP[BuDP] and H_2DTMSP[HDP] (Figure 6c) have variable slopes, in the 1.6–1.9 range. As with extraction of alkaline earth cations by these ligands, this suggests simultaneous extraction of a number of species. Attempts to calculate extraction constants for the extraction of Am(III) by H_2DTMSP[BuDP], through fitting the extraction data to equations similar to Eqs. (4)–(6), were unsuccessful due to the relative errors associated with the distribution ratio measurements and the speciation calculated from the VPO data and the number of different equilibria that must be considered. However, a qualitative understanding of the importance of the various sized H_2DTMSP[BuDP] aggregates in the extraction of

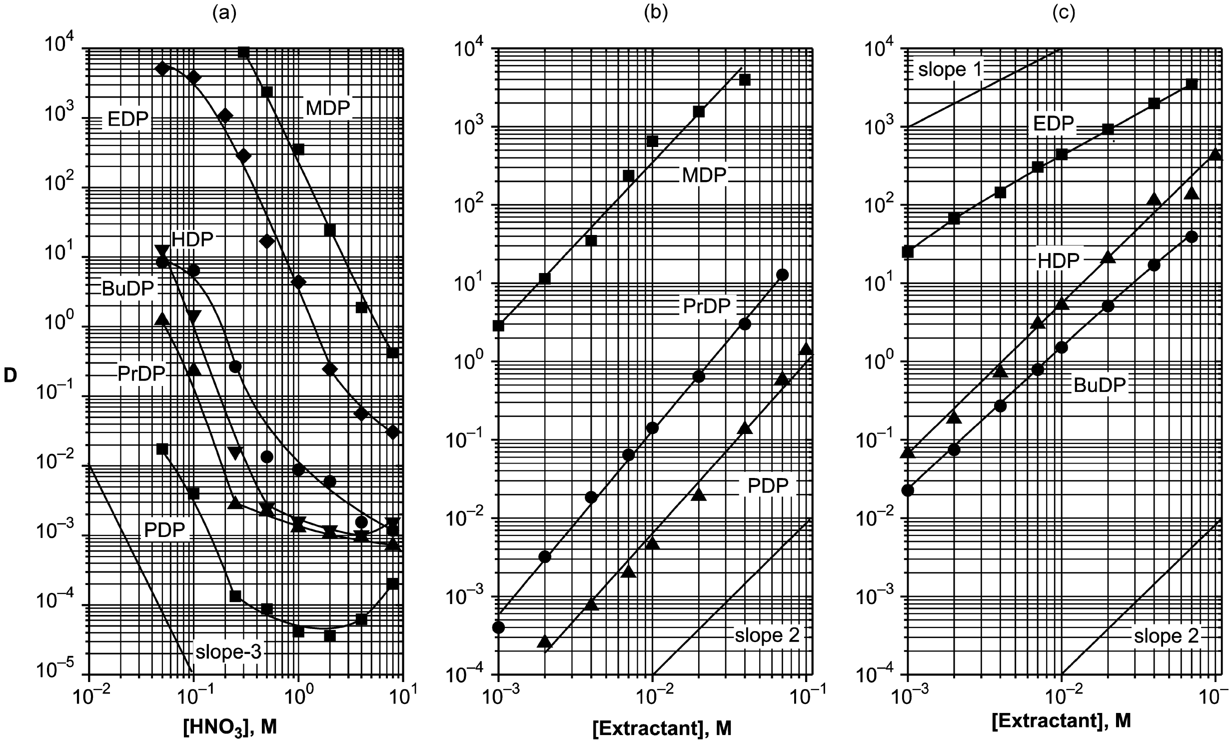


Figure 6. (a) Acid dependencies at 25°C for the extraction of Am(III) by 0.01 *M* H_2DTMSP[MDP], H_2DTMSP[EDP], H_2DTMSP[PrDP], H_2DTMSP[BuDP], H_2DTMSP[PDP], and H_2DTMSP[HDP] in *o*-xylene. (b) Extractant dependencies at 25°C for the extraction of Am(III) by H_2DTMSP[MDP] (from 1.0 *M* HNO_3), H_2DTMSP[PrDP] and H_2DTMSP[PDP] (from 0.1 *M* HNO_3). (c) Extractant dependencies at 25°C for the extraction of Am(III) by H_2DTMSP[EDP], H_2DTMSP[BuDP], and H_2DTMSP[HDP] (from 0.1 *M* HNO_3).

Am(III) can be obtained considering the VPO data and the variable slope of the extractant dependency data.

Since H_2DTMSP[BuDP] is primarily trimeric over the concentration range over which the extractant dependency was determined, the slope of approximately two suggests that Am(III) extraction occurs primarily via a species containing two H_2DTMSP[BuDP] trimers. At higher extractant concentrations, however, the concentration of hexameric H_2DTMSP[BuDP] becomes more important. Extraction via this hexameric aggregate would yield extractant dependencies of unity, which explains why the slope of the observed extractant dependencies exhibit a somewhat decreased slope at the highest extractant concentrations studied.

As with Ca extraction, the extractant dependency slope of approximately two observed for Am(III) extraction by H_2DTMSP[HDP] indicates that Am(III) is not primarily extracted by a single hexameric H_2DTMSP[HDP] aggregate. Vapor pressure osmometric data suggests that H_2DTMSP[HDP] is slightly less aggregated than H_2DTMSP[EDP]. Therefore, at a given extractant concentration, the concentration of the monomer is higher for H_2DTMSP[HDP] than for H_2DTMSP[EDP]. Even at the highest extractant concentrations employed in the solvent extraction experiments, monomeric H_2DTMSP[HDP] composes a significant portion ($\sim 25\%$) of the species present in the solution (Fig. 3b). In the H_2DTMSP[EDP] system, this relatively high concentration of monomer is observed only at the lowest extractant concentrations ($< 0.002\,M$). A substantial deviation of the extractant dependency from slope one 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 (26).

It is readily apparent from Fig. 6b that, of the ligands with an odd number of bridging methylene groups, H_2DTMSP[MDP] is the most efficient metal ion extractant, presumably due to the stability of the six-membered chelate rings formed upon metal ion complexation. As the number of bridging methylene groups is increased to three and five, the extraction of Am(III) becomes progressively less efficient, even though the basicity of the phosphoryl oxygens increases. This suggests that the chelate effect is the most important factor in determining metal ion extraction efficiency of this series of dimeric ligands. The larger chelate rings possible upon complexation of metal ions by H_2DTMSP[PrDP] and H_2DTMSP[PDP] are expected to be considerably less stable than the six-membered rings formed in H_2DTMSP[MDP] complexes (42). Additionally, as the distance between the phosphorus atoms of the extractants increase, they are more likely to behave as monofunctional ligands, with only one of the phosphorus groups complexing a given metal ion. This is evidenced by the tendency for H_2DTMSP[PrDP] and H_2DTMSP[PDP] to behave similarly to monofunctional extractants, extracting Ca^{2+} more efficiently than Sr^{2+}, Ba^{2+}, and Ra^{2+}, while H_2DTMSP[MDP] shows essentially no selectivity over the series of alkaline earth cations. Another factor that must be considered, however, is the decreased acidity of the POH groups as more methylene groups bridge the phosphorus atoms. Since the extraction of metal cations by these ligands is facilitated through charge neutralization by the displacement of these acidic protons, decreased acidity could result in decreased extraction efficiency.

In the case of the more highly aggregated extractants, the metal ion extraction efficiency does not correlate with the size of the chelate ring possible upon metal ion complexation or the expected acidity of the POH groups. H_2DTMSP[EDP] is the most efficient metal ion extractant followed by H_2DTMSP[HDP] and then H_2DTMSP[BuDP]. Here, the metal ion extraction efficiency correlates with the relative amount of hexameric aggregate present in the organic phase. H_2DTMSP[HDP] is a poorer extractant than H_2DTMSP[EDP], and has a β_6 which is a factor of two lower than that for H_2DTMSP[EDP]. H_2DTMSP[BuDP] is a still poorer extractant and exists primarily as trimeric aggregates in toluene, with hexameric H_2DTMSP[BuDP] becoming more prominent at higher extractant concentrations. Furthermore, the more highly aggregated extractants are more efficient metal ion extractants than the dimeric extractants (with the exception of H_2DTMSP[MDP], which is the most efficient extractant in this series due to the stability of the six-membered chelate rings formed upon metal ion complexation). This may be due to the ability of the more highly aggregated extractants to function as reverse micelles, with a central hydrophilic cavity containing the metal ion and the lipophilic esterifying groups oriented outward into the organic diluent (36).

Th(IV) and U(VI) Extraction

Solvent extraction data obtained for the extraction of Th(IV) and U(VI) metal cations with H_2DTMSP[PrDP] and H_2DTMSP[BuDP] suggest that these ligands behave similar to H_2DTMSP[MDP] and H_2DTMSP[EDP] and their di(2-ethylhexyl) analogs in the extraction of these metal cations (6–8,26). The extraction of Th(IV) and U(VI) indicates that these ions are extracted primarily by the fully protonated ligands, and tend to form complexes of varying stoichiometry with a tendency to polymerize.

CONCLUSIONS

The aggregation and solvent extraction properties of four novel silicon-substituted diphosphonic acids, *P*,*P*′-di[3-(trimethylsilyl)-1-propyl] propylene-, butylene-, pentylene-, and hexylene- diphosphonic acids have been compared to their methylene and ethylene homologs and to related di(2-ethylhexyl)-substituted diphosphonic acids. The behavior of H_2DTMSP[BuDP] was found to closely parallel that of its di(2-ethylhexyl) analog, primarily forming trimeric species in toluene at 25°C while extracting selected alkaline earth cations and representative tri-, tetra-, and hexa- valent actinides 2–3 times more efficiently. This provides further evidence that the addition of a silicon functionality does not adversely affect the solvent extraction properties of diphosphonic acid ligands.

As with the analogous 2-ethylhexyl-substituted alkylenediphosphonic acids, the number of methylene groups bridging the two phosphorus atoms of the ligands was found to dramatically affect the aggregation and solvent extraction properties of the silyl-substituted alkylenediphosphonic acids. From ^{31}P nuclear magnetic resonance spectroscopy, infrared spectroscopy, VPO, and distribution ratio measurements, it is evident that a number of factors, including the basicity of the P=O group, the acidity of the POH protons, the size of the chelate ring formed upon metal ion complexation, and the aggregation state of the ligand play roles of varying importance in determining the efficiency of metal ion extraction. H_2DTMSP[MDP] is the most efficient metal ion extractant in this series presumably due to the stability of the six-membered chelate rings formed upon metal ion complexation. The highly aggregated ligands, H_2DTMSP[EDP], H_2DTMSP[BuDP], and H_2DTMSP[HDP], are more efficient metal ion extractants than the dimeric H_2DTMSP[PrDP] and H_2DTMSP[PDP], suggesting that extraction via hexameric aggregates is more efficient than via dimeric aggregates. Work is now underway in this laboratory to more fully understand this phenomenon and to explore the relationship between the aggregation state of these ligands and their miscibility with liquid or supercritical CO_2.

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REFERENCES

1. Gatrone, R.C.; Horwitz, E.P.; Rickert, P.G.; Nash, K.L. The Synthesis and Decomposition of Novel Organophosphorus Complexants. Sep. Sci. Technol. **1990**, *25*, 1607–1627.

2. Nash, K.L.; Rickert, P.G. Thermally Unstable Complexants: Stability of Lanthanide/Actinide Complexes, Thermal Instability of the Ligands, and Applications in Actinide Separations. Sep. Sci. Technol. **1993**, *28*, 25–40.
3. Nash, K.L. *f*-Element Complexation by Diphosphonate Ligands. J. Alloys Compd. **1997**, *249*, 33–40.
4. Fugate, G.A.; Nash, K.L.; Sullivan, J.C. Kinetic Study of the Reactions of Np(V) and U(VI) with Diphosphonic Acids in Acetate Buffer Solutions. Radiochim. Acta **1997**, *79*, 161–166.
5. Nash, K.L. Thermodynamics of Formation of Complexes Between Thorium(IV) and Substituted Methane Diphosphonic Acids in Acidic Solutions. Radiochim. Acta **1991**, *54*, 171–179.
6. Chiarizia, R.; Horwitz, E.P.; Rickert, P.G.; Herlinger, A.W. Metal Extraction by Alkyl-Substituted Diphosphonic Acids. Part 1. *P*,*P*′-Di(2-Ethylhexyl) Methanediphosphonic Acid. Solvent Extr. Ion Exch. **1996**, *14*, 773–792.
7. Chiarizia, R.; Herlinger, A.W.; Horwitz, E.P. Metal Extraction by Alkyl-Substituted Diphosphonic Acids. Part 3. *P*,*P*′-Di(2-Ethylhexyl) Ethanediphosphonic Acid Solvent Extraction Study. Solvent Extr. Ion Exch. **1997**, *15*, 417–431.
8. Chiarizia, R.; Herlinger, A.W.; Cheng, Y.D.; Ferraro, J.R.; Rickert, P.G.; Horwitz, E.P. Metal Extraction by Alkyl-Substituted Diphosphonic Acids. Part 4. *P*,*P*′-Di(2-Ethylhexyl) Butanediphosphonic Acid. Solvent Extr. Ion Exch. **1998**, *16*, 505–526.
9. Horwitz, E.P.; Chiarizia, R.; Diamond, H.; Gatrone, R.C.; Alexandratos, S.D.; Trochimczuk, A.W.; Crick, D.W. Uptake of Metal Ions by a New Chelating Ion-Exchange Resin. Part 1: Acid Dependencies of Actinide Ions. Solvent Extr. Ion Exch. **1993**, *11*, 943–966.
10. Alexandratos, S.D.; Trochimczuk, A.W.; Crick, D.W.; Horwitz, E.P.; Gatrone, R.C.; Chiarizia, R. Synthesis and Ion-Complexing Properties of a Novel Polymer-Supported Reagent with Diphosphonate Ligands. Macromolecules **1996**, *29*, 1021–1026.
11. Chiarizia, R.; D'Arcy, K.A.; Horwitz, E.P.; Alexandratos, S.D.; Trochimczuk, A.W. Uptake of Metal Ions by a New Chelating Ion Exchange Resin. Part 8: Simultaneous Uptake of Cationic and Anionic Species. Solvent Extr. Ion Exch. **1996**, *14*, 519–542.
12. Chiarizia, R.; Horwitz, E.P.; D'Arcy, K.A.; Alexandratos, S.D.; Trochimczuk, A.W. Uptake of Actinides and Other Ions by Diphosil, a New Silica-Based Chelating Ion Exchange Resin. Spec. Publ.—R. Soc. Chem. **1996**, *182*, 321–328.
13. Chiarizia, R.; Horwitz, E.P.; D'Arcy, K.A.; Alexandratos, S.D.; Trochimczuk, A.W. Uptake of Metal Ions by a New Chelating Ion

Exchange Resin. Part 9: Silica Grafted Diphosphonic Acid. Solvent Extr. Ion Exch. **1996**, *14*, 1077–1100.

14. Chiarizia, R.; Horwitz, E.P.; Alexandratos, S.D.; Gula, M.J. Diphonix® Resin: A Review of Its Properties and Applications. Sep. Sci. Technol. **1997**, *32*, 1–35.
15. Chiarizia, R.; Horwitz, E.P.; Beauvais, R.A.; Alexandratos, S.D. Diphonix-Cs: A Novel Combined Cesium and Strontium Selective Ion Exchange Resin. Solvent Extr. Ion Exch. **1998**, *16*, 875–898.
16. Horwitz, E.P.; Chiarizia, R.; Dietz, M.L. Dipex: A New Extraction Chromatographic Material for the Separation and Preconcentration of Actinides from Aqueous Solution. React. Funct. Polym. **1997**, *33*, 25–36.
17. Phelps, C.L.; Smart, N.G.; Wai, C.M. Past, Present and Possible Future Applications of Supercritical Fluid Technology. J. Chem. Educ. **1996**, *73*, 1163–1168.
18. Brennecke, J. Department of Chemical Engineering, University of Notre Dame, Private communication, 2000.
19. De Simone, J.M.; Maury, E.E.; Menceloglu, Y.Z.; McClain, J.B.; Romack, T.J.; Combes, J.R. Dispersion Polymerizations in Supercritical Carbon Dioxide. Science **1994**, *265*, 356–359.
20. Lin, Y.; Brauer, R.D.; Laintz, K.E.; Wai, C.M. Supercritical Fluid Extraction of Lanthanides and Actinides from Solid Materials with a Fluorinated β-Diketones. Anal. Chem. **1993**, *65*, 2549–2551.
21. Dzielawa, J.A.; Thesis Dissertation, Loyola University Chicago, Chicago.
22. Griffith-Dzielawa, J.A.; Barrans, R.E.; McAlister, D.R.; Dietz, M.L.; Herlinger, A.W. Synthesis and Characterization of Di[3-(Trimethylsilyl)-1-propylene] Alkylenediphosphonic Acids. Synth. Commun. **2000**, *30*, 2121–2132.
23. Kendrick, T.C.; Parboo, B.; White, J.W.; The Chemistry of Organic Silicon Compounds, John Wiley and Sons: Chichester, UK, 1989; Vol. 2.
24. Herlinger, A.W.; McAlister, D.R.; Chiarizia, R.; Dietz, M.L. Aggregation, Metal Ion Extraction and Solubility Properties of Silyl-Substituted Alkylenediphosphonic Acids, Twelfth Symposium on Separation Science and Technology for Energy Applications, Gatlinburg, Tennessee, October 15–18, 2001.
25. Fink, R.; Beckman, E.J. Phase Behavior of Siloxane-Based Amphiphiles in Supercritical Carbon Dioxide. J. Supercrit. Fluids **2000**, *18*, 101–110.
26. McAlister, D.R.; Dietz, M.L.; Chiarizia, R.; Herlinger, A.W. Metal Extraction by Silyl-Substituted Diphosphonic Acids. Part 1. *P*,*P*′-Di[3-(Trimethylsilyl)-1-propylene] Methylene- and Ethylene-Diphosphonic Acids. Sep. Sci. Technol. **2001**, *36*, 3541–3562.
27. Yamamoto, M.; Iwai, Y.; Nakajama, T.; Arai, Y. Fourier Transform Infrared Study on Hydrogen Bonding Species of Carboxylic Acids in

Supercritical Carbon Dioxide with Ethanol. J. Phys. Chem. A **1999**, *103*, 3525–3529.

28. Lu, J.; Han, B.X.; Yan, H.K. Solvent Effect on Monomer-Dimer Equilibrium in Supercritical Fluid: Spectroscopic and Thermodynamic Studies. Phys. Chem. Chem. Phys. **1999**, *1*, 449–453.
29. McAlister, D.R.; Herlinger, A.W.; Ferraro, J.R.; Dietz, M.L.: Synthesis and Characterization of Metal Complexes of *P*,*P*′-Di[3-(Trimethylsilyl)-1-propyl] Methylenediphosphonic Acid. Synth. React. Inorg. Met.-Org. Chem. **2002**, *32*, in press.
30. Herlinger, A.W.; Chiarizia, R.; Ferraro, J.R.; Rickert, P.G.; Horwitz, E.P. Metal Extraction by Alkyl-Substituted Diphosphonic Acids. Part 2. *P*,*P*′-Di(2-Ethylhexyl) Ethanediphosphonic Acid Aggregation and IR Study. Solvent Extr. Ion Exch. **1997**, *15*, 401–416.
31. Moedritzer, K.; Irani, R.R. Synthesis and Properties of Mono- and Poly-Methylene Diphosphonic Acids and Esters. J. Inorg. Nucl. Chem. **1961**, *22*, 297–304.
32. Turanov, A.N.; Karandashev, V.K.; Yarkevich, A.N.; Kharitonov, A.V. Effect of the Structure of Phosphorylated Carboxylic Acids on Extraction of Uranium and Thorium from Nitric Acid Solutions. Radiochemistry **2000**, *42*, 251–256.
33. Rozen, A.M.; Krupnov, B.V. Dependence of the Extraction Ability of Organic Compounds on Their Structure. Usp. Khim. **1996**, *65*, 1052–1079.
34. Zalupski, P.R.; McAlister, D.R.; Stepinski, D.; Herlinger A.W. Substituent Inductive Effects on the Basicity of Phosphoryl Oxygens in Bisphosphonates. 2001, In preparation.
35. Barrans, R.E.; McAlister, D.R.; Herlinger, A.W.; Chiarizia, R.; Ferraro, J.R. Hydrogen Bonding in Aggregates of Dialkyl-Substituted Diphosphonic Acids and Monofunctional Analogues. Solvent Extr. Ion Exch. **1999**, *17*, 1195–1217.
36. Chiarizia, R.; Urban, V.; Thiyagarajan, P.; Herlinger, A.W. SANS Study of the Complexes Formed by Selected Metal Cations and *P*,*P*′-Di(2-Ethylhexyl) Ethane- and Butane- Diphosphonic Acids. Solv. Extr. Ion Exch. **1999**, *17*, 1171–1194.
37. Chiarizia, R.; Urban, V.; Thiyagarajan, P.; Herlinger, A.W. Aggregation of Complexes Formed in the Extraction of Selected Metal Cations by *P*,*P*′-Di(2-Ethylhexyl) Methanediphosphonic Acid. Solvent Extr. Ion Exch. **1999**, *17*, 113–132.
38. Irani, R.R.; Moedritzer, K. Metal Complexing by Phosphorus Compounds VI. Acidity Constants and Calcium and Magnesium Complexing by Mono- and Polymethylene Diphosphonates. J. Phys. Chem. **1962**, *66*, 1349–1353.

39. Eberson, L. Acidity and Hydrogen Bonding of Carboxyl Groups. *The Chemistry of Carboxylic Acids*; John Wiley and Sons Inc.: New York, 1969; 274–276.
40. Chiarizia, R.; McAlister, D.R.; Herlinger, A.W.; Bond, A.H. Solvent Extraction by Dialkyl-Substituted Diphosphonic Acids in a Depolymerizing Diluent. Part 1: Alkaline Earth Cations. Solvent Extr. Ion Exch. **2001**, *19*, 261–276.
41. Herlinger, A.W.; Ferraro, J.R.; Chiarizia, R.; Horwitz, E.P. An Investigation of P,P'-Di(2-Ethylhexyl) Methanediphosphonic Acid and Some of Its Metal Complexes. Polyhedron **1997**, *16*, 1843–1854.
42. Cotton, A.F.; Wilkinson, G. *Advance Inorganic Chemistry*, 5th Ed.; John Wiley and Sons, Inc.: New York, 1988; 45–47.

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