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METAL ION EXTRACTION BY SILYL-SUBSTITUTED DIPHOSPHONIC ACIDS. I. P,P'-DI-[3-(TRIMETHYLSILYL)-1-PROPYLENE] METHYLENE- AND ETHYLENEDIPHOSPHONIC ACIDS

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METAL ION EXTRACTION BY SILYL-SUBSTITUTED DIPHOSPHONIC ACIDS. I. P,P′-DI-[3-(TRIMETHYLSILYL)-1-PROPYLENE] METHYLENE- AND ETHYLENEDIPHOSPHONIC ACIDS

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ABSTRACT

In conjunction with efforts to develop novel actinide extractants that exhibit solubility in supercritical carbon dioxide ($SCCO_2$), the effect of adding silicon-based functionalities to diphosphonic acids on their aggregation and solvent extraction chemistry was investigated. Two silyl-derivatized diphosphonic acids, P,P′-di[3-(trimethylsilyl)-1-propylene] methylenediphosphonic acid (H_2DTMSP[MDP]) and P,P′-di[3-(trimethylsilyl)-1-propylene] ethylenediphosphonic acid (H_2DTMSP[EDP]), were prepared and their aggregation and metal ion extraction properties compared to those of the previously studied P,P′-di(2-ethylhexyl) alkylenediphos-

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phonic acids. Vapor pressure osmometry of H_2DTMSP[MDP] and H_2DTMSP[EDP] in toluene (25°C) indicates that, as is the case for the 2-ethylhexyl-substituted alkylenediphosphonic acid analogs, the compounds are dimeric and (primarily) hexameric, respectively, in the concentration range investigated. Distribution ratio measurements for the alkaline earth cations Ca^{2+}, Sr^{2+}, Ba^{2+}, and Ra^{2+} as well as the representative tri-, tetra-, and hexavalent actinides Am^{3+}, Th^{4+}, and UO_2^{2+} between solutions of H_2DTMSP[MDP] and H_2DTMSP[EDP] in *o*-xylene and nitric acid indicate that the behavior of these silyl-derivatized compounds closely mimics that of the analogous P,P′-di(2-ethylhexyl) alkylenediphosphonic acids, indicating that incorporation of a silyl functionality has no adverse impact on the metal ion extraction properties of diphosphonic acids.

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

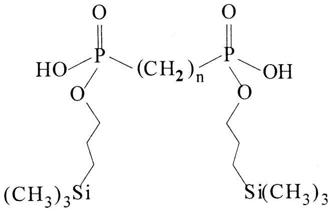
INTRODUCTION

Over the last decade, diphosphonic acids have attracted considerable interest as metal ion complexing agents (1–5). Previous work in our laboratory has demonstrated that these compounds form remarkably stable complexes in acidic media with a variety of metal ions (e.g., actinides, lanthanides, and Fe(III)), a result of the strong acidity of the diphosphonic acid functionality and its ability to chelate metal ions through either its phosphoryl or ionized phosphonic acid groups (5,6). Although originally developed for use as aqueous complexing (i.e., "hold-back" or stripping) agents (2,7), diphosphonic acid ligands have subsequently been shown to provide the basis of several novel chelating ion-exchange resins (8–14), and upon appropriate alkyl substitution, they act as powerful metal ion extractants applicable in both extraction chromatography (15) and conventional liquid-liquid extraction (6,15–17).

During the past several years, supercritical carbon dioxide ($SCCO_2$) has received increasing attention as an environmentally friendly alternative to conventional organic solvents (18) in extraction processes. Unlike many solvents, $SCCO_2$ does not decompose into ozone-depleting fragments or promote the generation of photochemical smog. In addition, the use of $SCCO_2$ can lead to reduced waste stream volumes; if the applied pressure is lowered sufficiently, the carbon dioxide will revert to the gaseous state, allowing dissolved solutes to be collected as a liquid or solid residue and the CO_2 to be collected, repressurized, and reused. Carbon dioxide offers a number of other significant advantages as a solvent, among them low cost, ready availability, comparatively low toxicity, favorable physical properties ($T_{crit} = 31.3°C$; $P_{crit} = 72.9$ atm), and in its supercritical state, relative ease of handling (using standard high-pressure equipment), low viscosity, and high diffusivity (18). Unfortunately, neither unsubstituted diphosphonic acids nor the alkyl-substituted acids reported to date (e.g., P,P′-di(2-ethylhexyl) alkylenediphosphonic acids (6)) are soluble in unmodified $SCCO_2$ (19) because of its low solvent power. Although the solvent power of $SCCO_2$ can be improved by addition of an organic modifier (e.g., methanol), this approach is not always effective. Moreover, mixtures of conventional solvents with $SCCO_2$ are clearly less environmentally benign than $SCCO_2$ alone. For this reason, much effort has been directed at the development of metal ion complexing agents/extractants that incorporate CO_2-philic substituents, which typically contain fluorine atoms or silicone polymer-based functionalities (20–31).

Recent work in our laboratory has focused on the preparation of diphosphonic acids that incorporate various silicon-based substituents (32) for possible application in $SCCO_2$ extraction. Such compounds are expected to be considerably less expensive than the analogous fluorinated diphosphonic acids, increasing the likelihood of eventual large-scale application. Moreover, while significant effort has been devoted to examination of the fluorination effect on metal ion complexation/extraction behavior and the $SCCO_2$ solubility of various ligands, relatively little work has been reported on the effect of adding silicon-based functional groups to the ligands. Until recently (32), no report had been made of an extant stable dialkyl alkylenediphosphonic acid that contained a silicon moiety.

As a first step in evaluating the potential utility of silicon-derivatized diphosphonic acids as metal ion extractants in $SCCO_2$, we have prepared 2 compounds containing the 3-(trimethylsilyl)-1-propyl group (Structure I, with n = 1 for H_2DTMSP[MDP] and n = 2 for H_2DTMSP[EDP]). Although our preliminary results indicated that the extractants are not appreciably soluble in $SCCO_2$, we evaluated their metal ion extraction and aggregation properties in toluene-*o*-xylene. In this way, the behavior of these compounds can readily be compared to that of conventional dialkyl alkylenediphosphonic acids (for which such data have been previously reported (6,16)) and the effect of the introduction of a silicon-



Structure I.

based functional group could be determined. The 3-(trimethylsilyl)-1-propyl group was selected for this work because the corresponding alcohol is commercially available and can be used to esterify diphosphonic acids through the use of well-established methodology (32). In addition, separating the trimethylsilyl functionality from the remainder of the molecule by 3 carbon atoms provides optimal chemical stability and synthetic accessibility (33).

EXPERIMENTAL

Materials

H_2DTMSP[MDP] and H_2DTMSP[EDP] were synthesized and characterized as described previously (32). The ligands were shown by potentiometric titration in methanol with standard base (J.T. Baker Chemical Co, Phillipsburg, NJ) to be greater than 97% pure. Sucrose octaacetate (Jupiter Instrument Co) and solutions prepared from Baker-analyzed PHOTREX grade toluene (Aldrich Chemical Co, Milwaukee, Wis) were used without further purification for the vapor pressure osmometry (VPO) measurements. Aqueous solutions were prepared with water from a Milli-Q2 purification system and Ultrex reagent nitric acid (J. T. Baker Chemical Co). The organic solutions used in solvent extraction experiments were prepared by dissolving a known mass of the extractant in sufficient *o*-xylene (Aldrich) to achieve the desired molarity. ^{45}Ca, ^{85}Sr, and ^{133}Ba were obtained from Isotope Products Laboratories (Burbank, Calif). ^{223}Ra was separated from ^{227}Ac through the use of an extraction chromatographic column that contained bis(2-ethylhexyl) phosphoric acid. The radioisotopes ^{241}Am, ^{233}U, and ^{230}Th were obtained from Argonna National Laboratory stocks. Only freshly purified ^{233}U and ^{230}Th were used in the extraction experiments. The radioisotopes were used at tracer level concentration, with the exception of ^{233}U and ^{230}Th, which were used in the solvent extraction experiments at a concentration of 10^{-5} to 10^{-4} mol/L.

Methods

The aggregation of H_2DTMSP[MDP] and H_2DTMSP[EDP] in toluene at 25°C was measured by VPO with a Jupiter Model 833 vapor pressure osmometer as described previously (34). The instrument was calibrated with standard toluene solutions of sucrose octaacetate. A plot of measured voltage versus sucrose octaacetate molality (m) gave a slope of 1788 μV/m for the instrument calibration constant.

The metal distribution ratios were measured as described for the di(2-ethylhexyl) alkylenediphosphonic acids (6,16,17). 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. Preliminary experiments showed that 5 minutes of vortexing was more than enough time to attain equilibrium. Duplicate experiments showed that the reproducibility of the *D* measurements was generally within 5%; however, the uncertainty interval was higher for the highest *D* values ($D > 10^3$).

RESULTS AND DISCUSSION

Aggregation

Figure 1 shows a comparison of the results of the VPO measurements for H_2DTMSP[MDP] and H_2DTMSP[EDP] with those for the monomeric standard sucrose octaacetate. As in the case of the analogous P,P′-di(2-ethylhexyl) methylenediphosphonic acid (H_2DEH[MDP]) (34), the VPO data indicate that H_2DTMSP[MDP] is dimeric in toluene at 25°C in the 0.01–0.12 m concentration range. The linearity of the data indicates that the aggregation constant is sufficiently large such that the extractant aggregation remains unchanged over the concentration range studied.

The VPO data for H_2DTMSP[EDP], in contrast to those observed for H_2DTMSP[MDP], are not linear. The best straight-line fit of the data has a slope

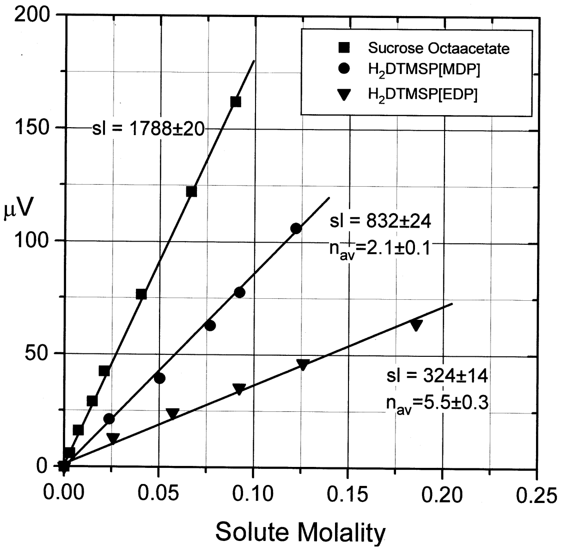


Figure 1. VPO measurements (microvolts, µV, vs. molality, m) with H_2DTMSP[MDP], H_2DTMSP[EDP], and the monomeric standard sucrose octaacetate in toluene at 25°C.

consistent with an average aggregation number (n_{av}) of approximately 5.5. This strongly suggests the formation of hexameric aggregates analogous to those observed for P,P′-di(2-ethylhexyl) ethylenediphosphonic acid (H_2DEH[EDP]) (34). For a more quantitative description of the aggregation equilibrium of H_2DTMSP[EDP] in toluene at 25°C, the VPO data are reported in Fig. 2a as the average degree of aggregation (n_{av}) versus the solute molality. The average degree of aggregation is defined as

$$n_{av} = \frac{C_{tot}}{S} = \frac{C_{tot}}{\left(\frac{\mu V}{K_r}\right)} \tag{1}$$

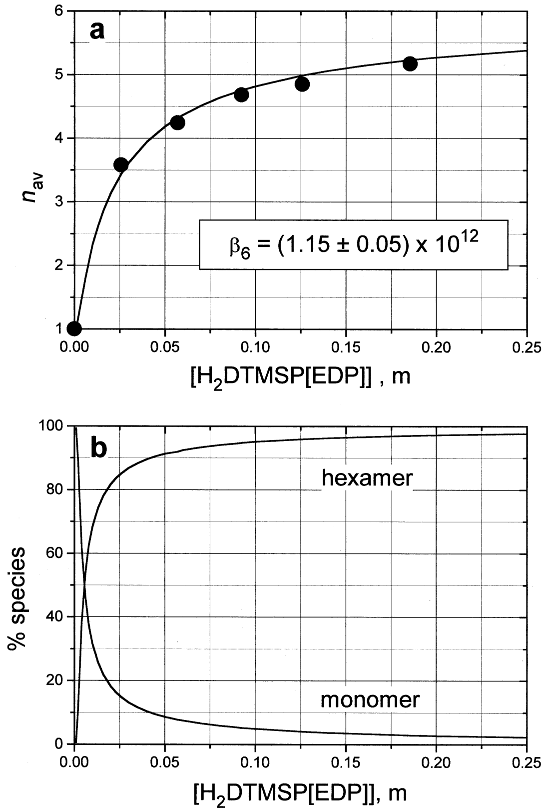


Figure 2. a) Best fit of aggregation data, average aggregation number (n_{av}) vs. molality (m), for H_2DTMSP[EDP]; b) Distribution of H_2DTMSP[EDP] between monomeric and hexameric species as a function of total solute concentration.

where C_{tot} is the known analytical concentration of H_2DTMSP[EDP], and S is the sum of the concentration of each species present in the system. For each data point in Fig. 1, an experimental value of S is obtained by dividing the instrument reading (μV) by the slope of the sucrose octaacetate reference line ($K_r = 1788$).

C_{tot} and S can be expressed through the following mass balance equations and equilibrium aggregation constants (β_n) :

$$C_{tot} = a + n \sum \beta_n a^n \tag{2}$$

$$S = a + \sum \beta_n a^n \tag{3}$$

where a represents the monomer concentration.

To calculate the β_n values that best describe the experimental values of Fig. 2a, the procedure and calculations described in (17) were used. Several aggregation models involving dimers, trimers, tetramers, and hexamers were tested. The results of the calculations indicate that the model that best describes the aggregation of H_2DTMSP[EDP] in toluene involves only the formation of a hexameric species with $\beta_6 = 1.15\ (\pm 0.05) \times 10^{12}$. A comparison of the experimental data with the calculated curve is shown in Fig. 2a.

The value of β_6 for H_2DTMSP[EDP] is more than one order of magnitude lower than that reported previously for H_2DEH[EDP] ($6(\pm 1) \times 10^{13}$ (16)). H_2DTMSP[EDP] thus has a somewhat lower tendency to aggregate than its 2-ethylhexyl analogue. Fig. 2b shows the species distribution diagram for H_2TMSP[EDP] in toluene calculated with the β_6 value reported above. It appears from the figure that, although the hexamer is the predominant species under most conditions, at very low extractant concentrations the presence of monomeric H_2DTMSP[EDP] is not negligible and must be taken into account to explain some features of the extraction data.

Solvent Extraction Studies

Alkaline Earth Cations

Figures 3 and 4 show the acid dependency data at 0.1 mol/L extractant and the extractant dependency data at 0.05 mol/L HNO_3 for selected alkaline earth cations with H_2DTMSP[MDP] and H_2DTMSP[EDP], respectively. These data indicate that these extractants behave very similarly to the analogous di(2-ethylhexyl) alkylenediphosphonic acid extractants (6,16). The acid dependencies for both extractants exhibit a slope of −2, which is consistent with the displacement of 2 protons by a divalent metal cation upon extraction into the organic phase.

The extractant dependencies for H_2DTMSP[MDP] show a variable slope. This slope is close to 2 in the 0.001–0.01 M concentration range and is slightly lower at higher extractant concentrations. This phenomenon was also observed

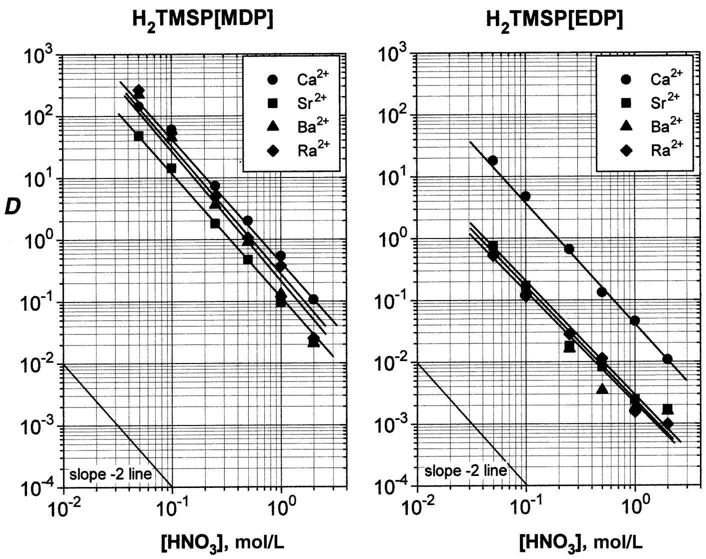


Figure 3. Acid dependencies at 25°C for the extraction of selected alkaline earth cations by 0.1 mol/L H_2DTMSP[MDP] and H_2DTMSP[EDP] in *o*-xylene.

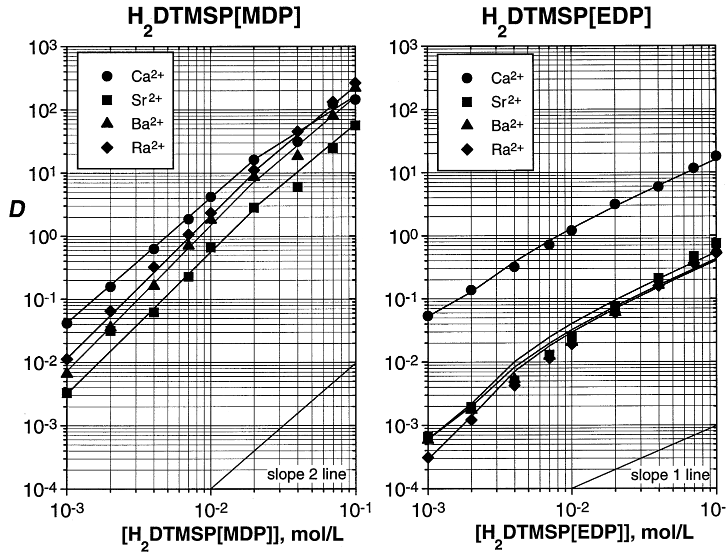


Figure 4. Extractant dependencies at 25°C for the extraction of selected alkaline earth cations by H_2DTMSP[MDP] and H_2DTMSP[EDP] in *o*-xylene from 0.05 mol/L HNO_3.

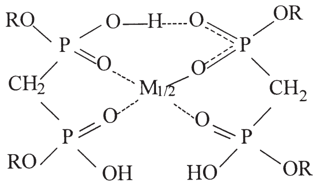
with H_2DEH[MDP] and was attributed to significant solubility of metal-ligand complexes in the aqueous phase (6). However, in the case of H_2DTMSP[MDP], the observed variation in the slope of the extractant dependency at higher extractant concentrations is smaller than that observed for H_2DEH[MDP]. This implies that the alkaline earth—H_2DTMSP[MDP] complexes are less soluble in the aqueous phase than are the analogous H_2DEH[MDP] complexes, a phenomenon which was also noted in qualitative solubility tests during the synthesis of H_2DTMSP[MDP] (35) and H_2DEH[MDP] (36) salts for study by infrared spectroscopy. The lower solubility of the silyl-substituted alkaline earth diphosphonic acid complexes in the aqueous phase may also explain why the extraction of alkaline earth cations by H_2DTMSP[MDP] or H_2DTMSP[EDP] yields *D* values that are typically 2 to 3 times higher than in alkaline earth extraction with H_2DEH[MDP] or H_2DEH [EDP], respectively, under identical conditions.

Because H_2DTMSP[MDP] has been shown by VPO to be dimeric in the concentration range over which the extractant dependencies were determined, the slope of approximately 2 for the extractant dependency indicates that each divalent alkaline earth cation is extracted by 2 H_2DTMSP[MDP] dimers. Therefore, as in the case of H_2DEH[MDP] (6), the stoichiometry of alkaline-earth cation extraction with H_2DTMSP[MDP] can be expressed as

$$M^{+} + 2(\overline{H_2Y})_2 \leftrightarrow \overline{M(HY \cdot H_2Y)_2} + 2H^{+} \qquad (4)$$

where overbars indicate organic phase species and H_2Y represents H_2DTMSP [MDP]. Structure II was proposed (6) for the extraction of alkaline earth cations by H_2DEH[MDP] and is very likely applicable for H_2DTMSP[MDP] as well. (For clarity, only one of the mono-deprotonated dimer units has been shown.) In this structure, 2 protons are displaced from 2 dimers of the extractant, as required by the slope analysis (i.e., −2 and 2 for the measured acid and extractant dependencies, respectively). The 6-member chelate rings shown in Structure II arise from the interaction of the metal ion with the phosphoryl oxygens of the extractant.

The extractant dependencies for H_2DTMSP[EDP] have a limiting slope of 1 in the 0.01–0.1 mol/L concentration range. As in the extraction of alkaline earth metals with H_2DEH[EDP], the slope increases at low extractant concentrations. A slope of 1 in the log-log plot of metal distribution ratio versus the analytical con-



Structure II.

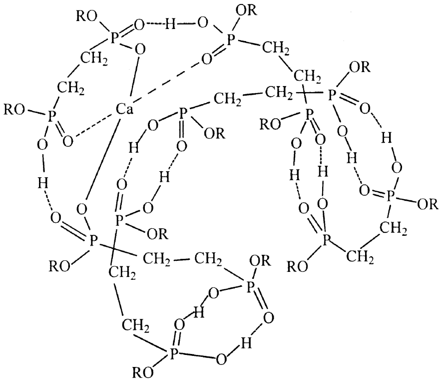
centration of the extractant is consistent with extraction by a highly aggregated species in which the aggregation is not disrupted by the metal ion (16). This result is in agreement with the VPO data, which indicate that H_2DTMSP[EDP] is primarily hexameric over the concentration range studied (Fig. 2b).

The extraction of alkaline earth cations by the H_2DTMSP[EDP] hexamer can therefore be expressed as

$$M^{2+} + (\overline{H_2Y})_6 \leftrightarrow \overline{MH_{10}Y_6} + 2H^+ \tag{5}$$

where $(\overline{H_2Y})_6$ is the hexameric H_2DTMSP[EDP] aggregate and $\overline{MH_{10}Y_6}$ is the metal-hexamer complex in the organic phase. As required by the slope of −2 in the acid dependency plot, 2 protons are lost by the hexamer upon complexation of an alkaline earth cation. Infrared spectroscopy (34) and small angle neutron scattering (37,38) experiments with H_2DEH[EDP] in toluene suggest a spherical morphology for the hexamer and the extracted alkaline-earth metal complexes (Structure III). 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 7- and 8-membered chelate rings are formed in this structure through coordination to the diphosphonate ligand. The remaining coordination sites on the metal ion may be occupied by water molecules, which are not shown for clarity. Although these experiments could not be repeated for H_2DTMSP[EDP] because of the low solubility of the metal complexes, we have made the reasonable assumption that the H_2DTMSP[EDP] aggregate adopts a similar structure.

The higher slope values in the 0.001–0.005 mol/L concentration range of the H_2DTMSP[EDP]—alkaline-earth extractant dependencies can be attributed to incomplete aggregation of the extractant. In this region, where the concentration of monomeric extractant is not negligible (Fig. 2b), the measured *D* values include contributions of both equilibrium (Eq. 5) and extraction by the monomeric ex-



Structure III.

Table 1. Equilibrium Constants for the Extraction of Alkaline Earth Cations by the Monomeric and Hexameric Forms of H_2DTMSP[EDP]

Cation	$K_{ex,mon}$	$K_{ex,hex}$
Ca	$(1.3 \pm 0.3) \times 10^{-1}$	$(2.49 \pm 0.05) \times 10$
Sr	$(1.4 \pm 1.4) \times 10^{-3}$	$(8.5 \pm 1.0) \times 10^{-2}$
Ba	$(1.4 \pm 1.4) \times 10^{-3}$	$(6.7 \pm 1.0) \times 10^{-2}$
Ra	$(7 \pm 7) \times 10^{-4}$	$(6.3 \pm 1.0) \times 10^{-2}$

Constants calculated from data of Fig. 4 and (Eqs. 5 and 6).

tractant. The reaction can be written as

$$M^{2+} + \overline{H_2Y} \leftrightarrow \overline{MY} + 2H^+ \tag{6}$$

Studies of metal ion extraction using *n*-decanol (39), a diluent in which the extractants are monomeric (40), verify that alkaline earth cations are readily extracted by monomeric diphosphonic acids.

The nonlinear least-squares curve-fitting feature of Origin® (Version 3.5, Microcal Software Inc, Northampton, Mass) was used to analyze the extractant dependency data for H_2DTMSP[EDP] given in Fig. 4. The best fit of the data was obtained using equilibria (Eqs. 5 and 6) and the β_6 value determined from the VPO data (Fig. 2a). We performed the calculations while under the assumption that the extent of extractant aggregation in toluene and *o*-xylene is the same and that all species behave ideally. The equilibrium constants provided by these calculations are reported in Table 1. The curves pictured in the H_2DTMSP[EDP] extractant dependency plot (Fig. 4) have been calculated using these equilibrium constants. The very high standard deviations obtained for $K_{ex,\ mon}$ stem from the few experimental points that are available in the extractant concentration range where reaction (Eq. 6) contributes significantly to the measured D values. Other stoichiometries for equilibrium (Eq. 6), such as that involving the extraction of the cation by 2 monomers of H_2DTMSP[EDP], provided a less satisfactory fit of the data.

As with the analogous di(2-ethylhexyl)-substituted extractants (6,16), the introduction of an additional CH_2 group into the alkylene bridge separating the phosphoryl groups profoundly affects alkaline earth extraction. H_2DTMSP[MDP] and H_2DEH[MDP] exhibit virtually no selectivity over the series of alkaline earths, while H_2DTMSP[EDP] and H_2DEH[EDP] behave in a manner similar to monofunctional extractants (41,42) and preferentially extract Ca. This behavior seems to indicate that the ethylenediphosphonic acids exhibit at least some monofunctional character.

Extraction of Ca with H_2DTMSP[EDP] yields D values typically 30 times higher than for Sr, Ba, or Ra. However, this selectivity is accompanied by lower D values than does extraction with H_2DTMSP[MDP]. Extraction with

H_2DTMSP[MDP] yields *D* values that are 10 times higher for Ca and 100 times higher for Sr, Ba, and Ra than those obtained in extraction with H_2DTMSP[EDP] under the same conditions. If one considers the proposed Structures II and III, the lower *D* values exhibited by H_2DTMSP[EDP] would be expected due to the formation of 7-member chelate rings rather than the more stable 6-member chelate rings formed by H_2DTMSP[MDP] (16).

Actinides

Figure 5 shows the nitric acid dependencies for the extraction of representative tri-, tetra-, and hexavalent actinides by 0.01 mol/L H_2DTMSP[MDP] and H_2DTMSP[EDP] solutions in *o*-xylene. These data are very similar to those observed for the di(2-ethylhexyl)-substituted diphosphonic acid extractants (6,16).

The acid dependency data for the extraction of Am(III) by H_2DTMSP[MDP] exhibit a maximum at 0.2–0.3 mol/L HNO_3. This feature of the data, which differs from the expected acid dependency for a trivalent metal cation (i.e., a straight line with a slope of -3), was also observed with the H_2DEH[MDP]-Am(III) system and could arise for several reasons. For example, species of different stoichiometries may be formed at different acid concentrations. In the 0.05–0.3 mol/L HNO_3 concentration range, a positively charged complex (e.g., 1:1 ligand-metal) could form

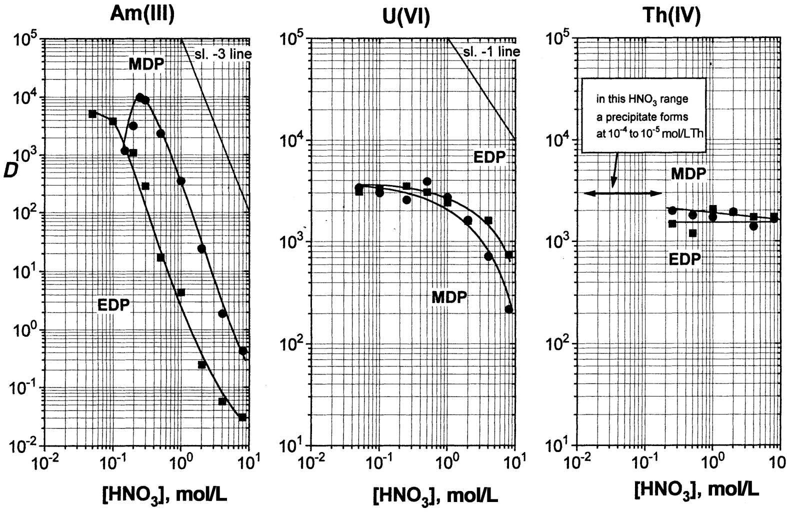


Figure 5. Acid dependencies at 25°C for the extraction of Am(III), U(VI), and Th(IV) by 0.01 mol/L H_2DTMSP[MDP] and H_2DTMSP[EDP] in *o*-xylene.

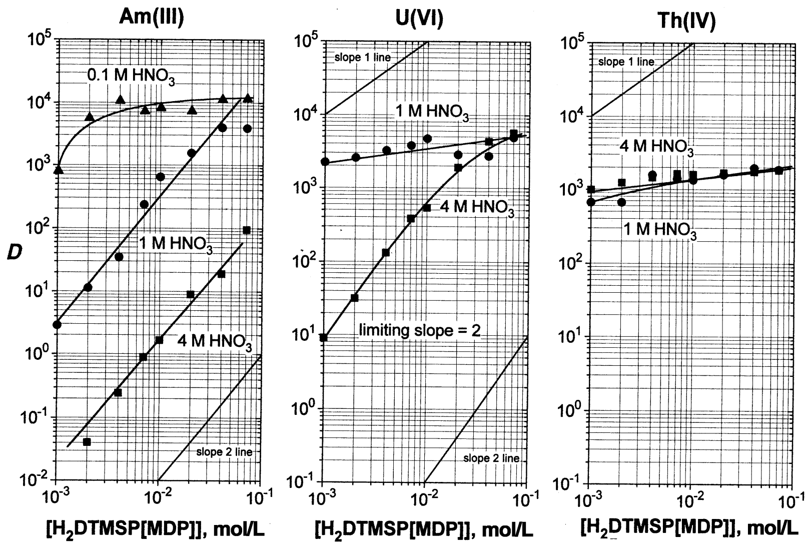


Figure 6. Extractant dependencies for the extraction of Am(III), U(VI), and Th(IV) by H_2DTMSP[MDP] in *o*-xylene from various concentrations (M = mol/L) of HNO_3.

and preferentially report to the aqueous phase. Extraction of this species into the organic phase would depend on the availability of the nitrate ion for charge neutralization. The value of the distribution ratio would therefore increase with nitric acid concentration. At higher acidities, a neutral complex (2:1 ligand-metal) that preferentially reports to the organic phase could be formed, leading to the expected acid dependency slope of -3. Alternatively, the formation of complexes with different degrees of protonation could be involved. At the lowest acidities, the ligand likely exists as the completely deprotonated dianion (DTMSP[MDP]$^{2-}$), while at higher acidities, the predominant ligand species would be the monoprotonated anion (HDTMSP[MDP]$^{1-}$). Because pK_a values for these diphosphonic acids are not available, we could not derive quantitative speciation information from the distribution data.

The possible formation of complexes with different ligand-to-metal stoichiometries is qualitatively supported by the extractant dependency data for H_2DTMSP[MDP] and Am(III) shown in Fig. 6. Extractant dependencies at 1 and 4 mol/L HNO_3, the acid concentration region in which the observed slope for the acid dependency plot is -3, exhibit slopes of 2. This indicates complexation by 2 H_2DTMSP[MDP] dimers from which 3 protons have been displaced to form complexes similar to Structure II. At 0.1 mol/L HNO_3, the extractant dependency data exhibit a slope of approximately 1 at low extractant concentrations, suggesting the formation of complexes of lower stoichiometry (i.e., a 1:1 ligand-metal complex). At higher extractant concentrations, the Am(III)-H_2DTMSP[MDP] distribution values at 0.1 mol/L HNO_3 are nearly constant, an observation consistent with significant aqueous phase solubility of the 1:1 ligand-metal complex. However, D values higher than 10^4 are subject to considerable uncertainty because the metal ion concentration in the aqueous phase is close to the detection limit normally achievable using reasonable amounts of radioactive tracers.

The acid dependency data observed for Am(III) extraction by H_2DTMSP [EDP] are closer to those expected for a trivalent cation (i.e., an observed slope of -3 over nearly the entire acid concentration range). At low acidities, the D values for the extraction of Am(III) by H_2DTMSP[EDP] (Fig. 5) exceed those for H_2DTMSP[MDP], while at high acidities D values are approximately 100 times lower for H_2DTMSP[EDP] than they are for H_2DTMSP[MDP]. As was the case for alkaline earth cations (see above), this behavior can be rationalized on the basis of 7-member chelate ring formation by H_2DTMSP[EDP] (Structure III), rather than the 6-member chelate rings possible with H_2DTMSP[MDP] (16).

The extractant dependency data for Am(III) at 1 and 4 mol/L HNO_3 with H_2DTMSP[EDP], shown in Fig. 7, exhibit slopes of 1 in the 0.01–0.1 mol/L concentration range. As observed for alkaline-earth cation extraction with this compound, at lower extractant concentrations (0.001–0.01 mol/L), the extractant de-

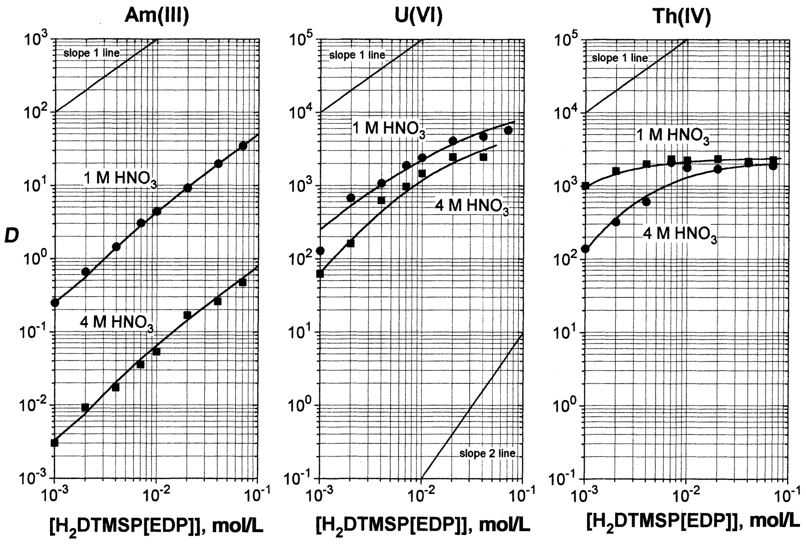


Figure 7. Extractant dependencies at 25°C for the extraction of Am(III), U(VI), and Th(IV) by H_2DTMSP[EDP] in *o*-xylene from 1 and 4 mol/L HNO_3.

Table 2. Equilibrium Constants for the Extraction of Am(III) by the Monomeric and Hexameric Forms of H_2DTMSP[EDP]

$[HNO_3]$, mol/L	$K_{ex,mon}$	$K_{ex,hex}$
1	$(1.8 \pm 0.3) \times 10^5$	$(2.55 \pm 0.05) \times 10^3$
4	$(1.4 \pm 0.5) \times 10^5$	$(2.16 \pm 0.08) \times 10^3$

Constants calculated from data of Fig. 7 and (Eqs. 7 and 8).

pendency data exhibit greater slopes due to incomplete ligand aggregation. In this region, both the monomeric and the hexameric species contribute to metal extraction according to the equilibrium equations

$$Am^{3+} + \overline{(H_2Y)_6} \leftrightarrow \overline{AmH_9Y_6} + 3H^+; \qquad K_{ex,\,hex} \tag{7}$$

and

$$Am^{3+} + \overline{2H_2Y} \leftrightarrow \overline{AmHY_2} + 3H^+; \qquad K_{ex,\,hex} \tag{8}$$

Through the procedure described above for the alkaline-earth cation extraction by H_2DTMSP[EDP], the β_6 value of H_2DTMSP[EDP] and equilibria (Eqs. 7 and 8) were used to fit the Am(III) extractant dependency data of Fig. 7. The values obtained for the equilibrium constants for Eqs. (7 and 8) are reported in Table 2. The curves shown in Fig. 7 for the Am(III) extractant dependencies were calculated using these values.

The data for U(VI) and Th(IV) extraction with H_2DTMSP[MDP] and H_2DTMSP[EDP] shown in Figs. 5–7 are very similar to those obtained with the analogous di(2-ethylhexyl) alkylenediphosphonic acids (6,16). Overall, the extraction data suggest that these metal complexes have a pronounced tendency to polymerize and exist in solution as a mixture of complexes with various stoichiometries and degrees of ligand protonation. The limited (U(VI)) or complete lack (Th(IV)) of acid dependency shown in Fig. 5 suggest that extraction of these metal ions by H_2DTMSP[MDP] and H_2DTMSP[EDP] occurs primarily through the phosphoryl oxygens of the fully protonated extractant. The U(VI) data show some acid dependency at higher acidities, where the slope approaches unity, suggesting partial deprotonation of the extractant and/or competition for the phosphoryl group from HNO_3.

The extractant dependency data for U(VI) exhibit variable slopes. At 4 mol/L HNO_3, the dependencies for H_2DTMSP[MDP] and H_2DTMSP[EDP] exhibit limiting slopes of 2 and 1, respectively. At 1 mol/L HNO_3, the slope decreases slightly for H_2DTMSP[EDP], while the H_2DTMSP[MDP] data become almost independent of the extractant concentration. Slope values close to unity are expected for the U(VI)-H_2DTMSP[EDP] extractant dependency data because the extractant is highly aggregated (16). Although the U(VI) data exhibit a limiting

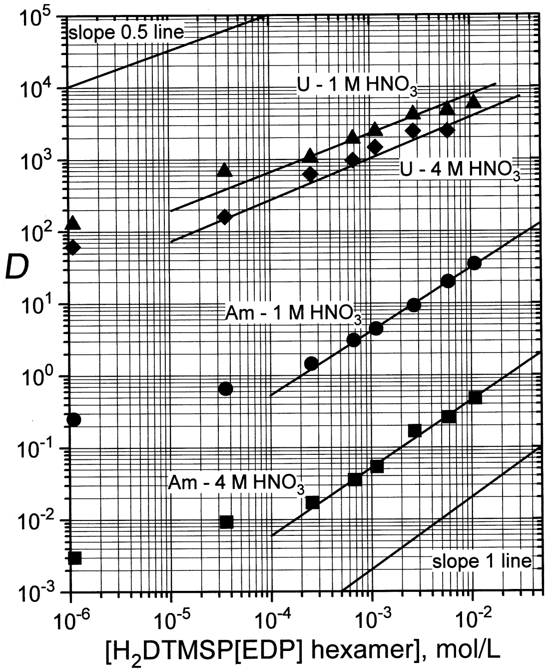


Figure 8. Distribution ratio, *D*, vs. hexamer concentration for the extraction of Am(III) and U(VI) at 25°C by H_2DTMSP[EDP] in *o*-xylene from 1 and 4 mol/L HNO_3.

slope of unity at low H_2DTMSP[EDP] concentration, the slope decreases at higher extractant concentrations.

To gain further insight into the U(VI)-H_2DTMSP[EDP] system, the extractant dependency data of Fig. 7 were plotted in Fig. 8 as a function of the H_2DTMSP[EDP] hexamer concentration. At each analytical concentration of the extractant, the hexamer concentration was calculated with the β_6 value of H_2DTMSP[EDP]. The Am(III) data are also shown in Fig. 8 to contrast the behavior of these 2 actinide ions. The Am(III) data are linear with a slope of unity, except at very low extractant concentrations, where extraction by monomeric H_2DTMSP[EDP] contributes significantly to the measured *D* values. The U(VI) data are also linear, but exhibit slopes of only 0.5. This slope is consistent with Eq. (9):

$$2UO_2^{2+} + \overline{(H_2Y)_6} \leftrightarrow \overline{(UO_2)_2H_{11}Y_6^{3+}} + H^+ \qquad (9)$$

and implies that 2 uranyl ions are extracted by each hexameric aggregate. As depicted in this equation, a single proton is displaced from the hexamer, which is consistent with the slope one observed from 1 to 4 mol/L HNO_3 in the H_2DTSMP[EDP] acid dependency plots. The remaining charge on the uranyl complex would be neutralized by nitrate anions. The lines fitting the U(VI) data of Fig. 8 were calculated based on equilibrium (Eq. 9) with values for the equilibrium constant equal to 4.0 ($\pm$0.5) $\times$ 10^4 at 1 mol/L HNO_3 and 6.0 ($\pm$1.0) $\times$ 10^4 at 4 mol/L HNO_3, respectively. In Fig. 8, the positive deviation of the U(VI) data from the calculated lines at the lowest extractant concentrations may be attributed to metal extraction by the monomeric extractant. However, the deviation from linearity is less pronounced than it is for Am(III), undoubtedly due to the much higher affinity of the monomeric extractant for U(VI).

The extraction of Th(IV) by H_2DTMSP[MDP] and H_2DTMSP[EDP] is independent of extractant concentration. This behavior is indicative of the formation of a new phase (a colloidal phase or a precipitate) in the extraction system. Under these conditions, the system becomes zerovariant. During collection of the acid dependency data of Fig. 5, this new phase manifested itself, at aqueous acidities below 0.2 mol/L, as cloudiness in the aqueous phase. This cloudiness most likely arises from precipitation of a Th(IV)-diphosphonate complex. Similar observations were noted with the di(2-ethylhexyl) analogues (6,16). The tendency of Th(IV) to form large polymeric aggregates with H_2DEH[MDP] in the organic phase was previously established through small-angle neutron scattering measurements (38), and H_2DTMSP[MDP] appears to exhibit the same behavior.

CONCLUSIONS

The aggregation and solvent extraction properties of 2 novel silicon-substituted diphosphonic acids, H_2DTMSP[MDP] and H_2DTMSP[EDP], were found to closely mimic those of analogous di(2-ethylhexyl) alkylenediphosphonic acids. As observed for di(2-ethylhexyl)-substituted extractants, the introduction of an additional CH_2 group into the alkylene bridge separating the phosphoryl groups profoundly affects the aggregation and solvent extraction properties of these silyl-substituted alkylenediphosphonic acids. VPO studies in toluene at 25°C indicate that H_2DTMSP[MDP] and H_2DTMSP[EDP] are dimeric and (primarily) hexameric, respectively, over the concentration range studied. Nonlinear least-squares fitting of the VPO data for H_2DTMSP[EDP] yielded an estimated aggregation equilibrium constant (β_6) of 1.15 ($\pm$ 0.05) $\times$ 10^{12}.

Extraction of alkaline earth cations from nitric acid into *o*-xylene solutions of the 2 extractants yields acid dependencies exhibiting slopes of -2 for both compounds and extractant dependencies of slope 2 and 1 for H_2DTMSP[MDP] and H_2DTMSP[EDP], respectively. These results suggest that the extraction of alkaline earth cations by H_2DTMSP[MDP] involves 2 mono-deprotonated dimers, while extraction by H_2DTMSP[EDP] involves a doubly deprotonated hexamer.

While H_2DTMSP[MDP] exhibits no selectivity over the series of alkaline earth cations studied, H_2DTMSP[EDP] preferentially extracts Ca over Sr, Ba, and Ra, much like a monofunctional organophosphorus extractant. The lower distribution ratios observed for alkaline earth extraction by H_2DTMSP[EDP] can be attributed to the formation of 7-member chelate rings, which are expected to be much less stable than the 6-member chelate rings possible with H_2DTMSP[MDP].

Extraction of Am(III) with H_2DTMSP[MDP] yields an acid dependency with a maximum at 0.2–0.3 mol/L HNO_3 and extractant dependencies in which slopes vary with acidity. This unusual behavior was attributed to the formation of positively charged species at low acidity that report preferentially to the aqueous phase. Extraction of Am(III) with H_2DTMSP[EDP] yields an acid dependency with a slope of -3 and an extractant dependency of unit slope, indicating complexation by a hexameric aggregate of H_2DTMSP[EDP] from which 3 protons have been displaced.

U(VI) and Th(IV) extraction with H_2DTMSP[MDP] and H_2DTMSP[EDP] exhibit little or no acid dependency, suggesting that metal complexation in these cases occurs predominantly through the interaction of the metal ion with the phosphoryl oxygens of the fully protonated extractant. The variable slopes exhibited by the U(VI) extractant dependency data suggest the formation of complexes of various stoichiometries and degrees of protonation, while the lack of extractant dependency exhibited by the extraction of Th(IV) indicates the formation of colloidal or solid species.

Taken together, these results clearly demonstrate that incorporation of a silicon-based functionality into a diphosphonic acid does not adversely affect its metal ion extraction behavior. Although our preliminary results indicate that the extractants considered here are not appreciably soluble in $SCCO_2$ (19), we expect that this can be remedied by use of an appropriate phase modifier or introduction of additional functional groups onto the diphosphonic acid backbone. Work addressing these opportunities is now underway in our laboratory.

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