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Stability Constants for Europium(III) Complexes with Substituted Methane Diphosphonic Acids in Acid Solutions

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Abstract

The stability constants of europium complexes with methane diphosphonic (MDPA), ethane-1,1-diphosphonic (EDPA), 1-hydroxyethane-1,1-diphosphonic (HEDPA), vinylidene-1,1-diphosphonic (VDPA) and 1,2-dihydroxyethane-1,1-diphosphonic (DHEDPA) acids were determined by solvent extraction distribution experiments in 2.0 M Na/HNO_3 media at 25 °C. The protonation constants for these tetrabasic acids were also determined by potentiometric titration. The latter two diphosphonic acids have not been previously reported in the open literature. Stability constants for a variety of protonated complexes with M:L stoichiometries varying from 1:1 to 1:3 are indicated in the least-squares analysis of the distribution data. Calculations based on the thermodynamic data indicate that diphosphonic acids are superior complexing agents for europium compared to carboxylic acids and aminopolycarboxylic acids in solutions of acidity greater than 0.01 M. The implication of these complexes for possible applications in separation processes is discussed.

Introduction

Among the strongest known complexing agents for the trivalent lanthanide ions are oxalic acid and the aminopolycarboxylic acids. These complexants have found a number of applications in processing of rare earth metal ions and in nuclear waste processing. The available thermodynamic data [1, 2] indicate that they are most effective at total acid concentrations below 0.01 M. In solutions of higher acidity, the ligand protonation equilibria become dominant over metal complex formation. An additional complicating feature of the aminopolycarboxylates, in this age of ever increasing environmental awareness, is their remarkable persistence in the environment. Aminopolycarboxylates have been established as significant promoters of radionuclides mobility from waste disposal sites [3].

In liquid–liquid extraction processes acidities greater than 0.1 M are commonly encountered. A complexing agent which functions in solutions of moderate to high acidity could find applications in nuclear waste processing schemes as a solvent cleanup reagent to assist in the decontamination of the organic solvent when solvent recycle is important. Another significant application would be as a 'hold-back' reagent to preferentially complex the polyvalent metal ion in the aqueous phase to permit enhanced selectivity for less extractable metal ions.

In an attempt to achieve the goal of improved extraction selectivity through adjustment of the aqueous phase without creating new environmental/disposal problems, we have begun our investigation of the complexing behavior and metal complex solubility of commercially available diphosphonic acids, and have synthesized previously unknown analogue compounds. Our goal in this investigation is to design a new class of compounds with the following combination of properties:

(1) they should form strong complexes with polyvalent metal ions in solutions of acidities greater than 0.01 M.

(2) both the complexant and its metal complexes should have sufficient solubility to function in continuous operation in a solvent extraction process

(3) they should be readily decomposable into innocuous (or relatively less hazardous) materials upon heating in the presence of mild oxidizing agents

Substituted methane diphosphonic acids were selected for investigation because previous studies of their protonation indicated that they are stronger acids than analogous carboxylic acids [4–8]. Known complexes of alkaline earth and divalent transition metal ions with substituted methane diphosphonic acids are considerably stronger than those of typical carboxylic acids with these metal ions [5, 7, 9–15]. Because the metal–ligand interaction for hard base donors is primarily electrostatic, the binding of polyvalent metal ions is expected to exceed that of the alkaline earths by a significant amount. The

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limited amount of data available on the stability of trivalent lanthanide/actinide complexes with related monophosphonic acid compounds is consistent with this expectation [16, 17].

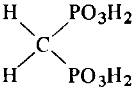
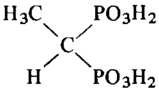
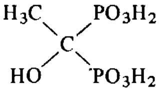
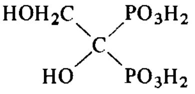
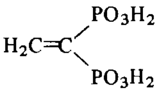
It was decided to investigate the thermodynamics of europium complexation because the trivalent lanthanides are reliable analogues for the trivalent actinides, which are most often the limiting species for successful separation of the transuranium elements. In this communication the protonation and europium complex formation of the subject diphosphonic acids are discussed and the potential application of these complexants in separation processes is considered.

Experimental

The structural formulae, full names and acronyms for the diphosphonic acids investigated are shown in Table 1. All materials were of reagent grade and were further purified by recrystallization of the acids or sodium salts. Methane diphosphonic acid (MDPA) was purchased from Aldrich as the acid and used without further purification. This material titrated at >99% purity. 1-Hydroxyethane-1,1-diphosphonic acid (HEDPA) was purchased as a 70% aqueous solution from Alfa and purified by recrystallization from glacial acetic acid [15]. The resulting product was a white crystalline powder which titrated as a monohydrate (consistent with the literature). NMR spectra of this compound confirmed this analysis and the absence of acetic acid in the solid product. Ethane-1,1-diphosphonic acid (EDPA) was also purchased from Alfa and was purified by dissolution of the white crystalline solid in deionized water, filtration to remove insoluble detritus, and recrystallized from water. The resulting white crystalline powder titrated at >99% purity.

Vinylidene-1,1-diphosphonic acid (VDPA) was synthesized as the tetra-sodium salt from HEDPA. The white crystalline solid was purified by multiple recrystallization from methanol–water mixtures and dried in a vacuum oven. This material titrated as a 10.5 hydrate, confirmed by Karl Fisher titration. Details of the synthesis, NMR spectroscopy and thermal degradation of this and the following compound are the subject of a companion paper [18]. 1,2-Dihydroxyethane-1,1-diphosphonic acid (DHEDPA) was synthesized from the VDPA and provided as a 2.1 M solution of the trisodium salt in deionized water. An attempt to recrystallize this diphosphonic acid from acetic acid resulted in decomposition of the DHEDPA. The stock solution was therefore used without further treatment and was stored with refrigeration. ^{31}P NMR analysis indicated 95% purity for this solution with the remaining phosphorus present as phosphoric acid and pyrophosphate. The presence of inorganic phosphorus species was accounted for in the least-squares analysis of the distribution and titration data.

TABLE 1. The substituted methane diphosphonic acids

Structure	Name	Acronym
	methane diphosphonic acid	MDPA
	ethane-1,1-diphosphonic acid	EDPA
	1-hydroxyethane-1,1-diphosphonic acid	HEDPA
	1,2-dihydroxyethane-1,1-diphosphonic acid	DHEDPA
	vinylidene-1,1-diphosphonic acid	VDPA

The extractant used for europium complexation studies was bis(2-ethylhexyl)phosphoric acid (HDEHP). The HDEHP was purchased from Kodak as a 98% pure reagent and used without further purification. The diluent carbon tetrachloride was analytical reagent grade from J. T. Baker and also used without purification.

$^{152-154}$Eu tracer was taken from laboratory stocks and prepared for use by sequential treatment with Ultrex $HClO_4$, HNO_3, deionized water, and finally dissolved in 0.001 M HNO_3. This procedure was repeated periodically to regenerate this stock and destroy unidentified solid material which appeared in the stock tracer solution after a time. All radiometric analysis was done by γ-counting in a Beckman Biogamma II instrument.

Potentiometric titrations were performed at 25 °C and 2.0 M total ionic strength, adjusted with $NaNO_3$. Carbon dioxide was excluded by conducting all titrations under a blanket of N_2. An Orion/Ross semi-microelectrode and Beckman Φ71 pH meter were used for all titrations. Measured pH was converted to hydrogen ion concentration using pH–pC_h calibration curves generated from either HNO_3–NaOH titrations at 2.0 M total ionic strength, or via pH measurement of solutions of acid concentration known by indicator titration. Titrations of the diphosphonic acids were performed at concentrations high enough to adequately define the first pK_a, and from both forward and reverse directions. At least three replicate titrations were done for each system.

Previous investigators have demonstrated complexation (ion association) of sodium ion by diphosphonic acids [4, 9], but such ion pairs are significant only in media of pH greater than 5 and so were not considered important in the present investigation. It should be noted for comparative purposes that the existence of such ion pairs primarily effects the values for the first protonation constants of the diphosphonic acids. Choppin *et al.* [19] have reported a significant specific cation effect in the complexing of europium by nitrate. To avoid the added uncertainty generated by such effects, we elected to use $NaNO_3$ as the supporting electrolyte rather than the non-complexing tetramethylammonium nitrate used in the previous investigations.

Europium–diphosphonate complex stability was determined by the standard method of Schubert [20]. The lowering of the distribution ratio in the solvent extraction of europium by HDEHP in CCl_4, due to complexation of europium in the aqueous phase, was determined as a function of total complexant concentration and acidity within the limits 0.1 to 0.01 M. A series of experiments at constant acidity and varying concentration of the complexant were performed for each system. Complete replicate experiments were run for each set of conditions. Equilibrium for both the solvent extraction reaction and the aqueous complexation reactions is achieved rapidly. One hour contact with intermittent mixing was sufficient for attainment of equilibrium under all conditions. The total concentrations of the complexant and the extractant were manipulated to provide distribution ratios in the range 10 to 0.01. These experiments were also performed at varying europium concentrations to confirm the absence of polynuclear complexes.

Results

Examples of the titration curves for each of the five acids are shown in Fig. 1. The pC_h–volume data sets (110–180 data pairs/titration) were transformed into a standard $\bar{p}$ (average proton number) relationship [21] from known concentrations of the titrant, the titrated acid (or sodium salt), [NaOH] or [HNO_3] added initially, and the volumes (initial and added). The concentrations of the diphosphonic acids were determined using the Gran plots of the multiple equivalence points observed in the titrations. Concentrations of the diphosphonic acid and the titrant were adjusted so that the volume increase during titration was kept below 20%. Additivity of volumes was assumed. Ionic strength variations during titration were minimal.

The relationship between $\bar{p}$(exp) and the concentrations of the protonated ligand species is shown in eqn. (1).

$$\bar{p}(\mathrm{exp}) = \frac{\sum_{h=0}^{4} h[\mathrm{H}_h\mathrm{L}]}{\sum_{h=0}^{4} [\mathrm{H}_h\mathrm{L}]} \tag{1}$$

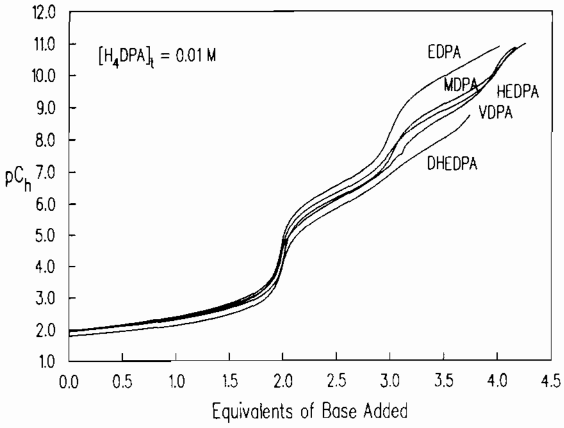


Fig. 1. Representative titration curves for MDPA, EDPA, VDPA, HEDPA and DHEDPA at 0.01 M total diphosphonic acid.

The concentrations of the protonated species are defined in terms of the ligand protonation equilibria, as illustrated in eqn. (2).

$$H^+ + H_{(h-1)}L^{(h-1-4)} \rightleftharpoons H_hL^{(h-4)},$$

$$K_{ah} = \frac{[H_hL^{(h-4)}]}{[H^+][H_{(h-1)}L^{(h-1-4)}]} \qquad (2)$$

These constants are for consecutive protonation equilibria (the h subscript corresponds to the number of protons bound to the L^{4-} species). As the fit equation requires overall protonation relationships, the combined equation takes the form given in eqn. (3).

$$\bar{p} = \frac{\sum_{h=0}^{4} \left\{ h \prod_{i=i}^{h} (K_{ai})[H^+]^h[L^{4-}] \right\}}{\sum_{h=0}^{4} \left\{ \prod_{i=i}^{h} (K_{ai})[H^+]^h[L^{4-}] \right\}} \qquad (3)$$

where $\Pi(K_{ai})$ is the product of the appropriate protonation constants. The free ligand concentration ($[L^{4-}]$) cancels out of this expression and the equation reduces to a relatively simple form with four fit parameters, $K_{a(1-4)}$.

Least-squares analysis of both the titration data and the distribution ratio data was accomplished using a program written by one of us (K.L.N.). This program is a generic Newton–Raphson iterative program described previously [22]. The fit equations and calculational details of the BASIC program were modified to fit each of the two different types of data (potentiometric and distribution) separately. The acidity constants of the diphosphonic acids were computed as the weighted mean of the parameters fit by the least-squares analysis of the titrations for each diphosphonic acid.

The protonation constants for the diphosphonic acids are summarized in Table 2 along with literature values for oxalic, phosphoric and pyrophosphoric acids [23]. The $\log(K_{a4}K_{a3})$ values at the far right of the Table (representing the equilibrium $2H^+ + H_2L^{2-} \rightleftarrows H_4L$ for the diphosphonic and pyrophosphoric acids, $2H^+ + HL^{2-} \rightleftarrows H_3L$ for phosphoric, $2H^+ + L^{2-} \rightleftarrows H_2L$ for oxalic acids) indicate the relative acidity of the dianions of these compounds. On the basis of this comparison, the diphosphonic acids are clearly stronger than either oxalic or phosphoric acids, comparable to pyrophosphoric acid. The comparison of the diphosphonic acids and carboxylic acid complexants is discussed in more detail below.

The stoichiometry of the two phase extraction reaction is shown in eqn. (4).

$$Eu^{3+} + 3(HD)_{2(o)} \rightleftharpoons Eu(DHD)_{3(o)} + 3H^+ \qquad (4)$$

where $(HD)_2$ is the well known dimer of HDEHP. The species present in the organic phase are indicated by the subscript (o). The equilibrium constant (standard state is 2.0 M Na/HNO_3, 25 ℃) for this reaction is given by:

$$K_{ex} = \frac{[Eu(DHD)_3]_{(o)}[H^+]^3}{[Eu^{3+}][(HD)_2]^3_{(o)}} \qquad (5)$$

The ratio of metal ion concentration in the organic to that in the aqueous phase is defined as D.

$$K_{ex} = \frac{D[H^+]^3}{[(HD)_2]^3_{(o)}} \qquad (6)$$

The extraction reaction has been investigated in a variety of diluents and the stoichiometry given above is well established. The average value for K_{ex} determined in the present experiments is 0.438(±0.022), in reasonable agreement with literature results for this system [24].

In the europium distribution experiments, we assume that only the extraction equilibrium outlined above is important, that is, no Eu–DPA complexes are extracted into the organic phase. The distribution of europium in the absence of diphosphonic acid is

TABLE 2. Protonation constants for diphosphonic acids

	$\log K_{a4}$	$\log K_{a3}$	$\log K_{a2}$	$\log K_{a1}$	$\log K_{a4}K_{a3}$
HEDPA	1.56(0.01)	2.20(0.01)	6.20(0.01)	9.12(0.01)	3.76
VDPA	1.41(0.01)	2.06(0.01)	6.01(0.02)	8.60(0.01)	3.47
DHEDPA	1.00(0.01)	1.65(0.01)	5.76(0.02)	7.80(0.01)	2.65
EDPA	1.43(0.01)	2.48(0.01)	6.56(0.01)	9.93(0.01)	3.91
MDPA	1.30(0.01)	2.35(0.01)	6.34(0.01)	8.90(0.01)	3.65
H_2Ox [a, b]	1.04	3.55	n.a.	n.a.	4.59
H_3PO_4 [b]	1.7	6.46	10.8	n.a.	9.16
$H_4P_2O_7$[b]	0.8	1.4	5.41	7.43	2.2

[a] H_2Ox is oxalic acid. [b] Standard state: 25 °C, I = 1.0 M from ref. 23. Numbers in parentheses represent the 2σ uncertainty limit.

corrected for a 1:1 europium nitrate complex (using stability constants from ref. 19, slightly altered to account for the ionic strength difference) and defined as D_o. As trivalent europium is not appreciably hydrolyzed below pH 5 [25], it is not necessary to include any modification to the fit equation for this effect. In the pH 1–2 range investigated the free diphosphonic acid ligand is distributed among the species H_4L, H_3L^- and H_2L^{2-}. The species HL^{3-} and L^{4-} are insignificant in this region. Analysis of the distribution data also indicates that the final two protons are not lost upon complex formation. To simplify the equations and to facilitate comparisons with carboxylic acids below, we shall define the diprotonated diphosphonic acid ligand (H_2L^{2-}) as X^{2-}. (The thermodynamic parameters in Table 4 are defined on this basis.) Equation (7) is the basic equation used to fit the distribution data,

$$D = \frac{K_{ex}[(HD)_2]^3/[H^+]^3(1+\beta_{NO_3}[NO_3^-])}{(1+\beta_{NO_3}[NO_3^-]+\Sigma(\beta_{mhx}[H]^h[X^{2-}]^x))} \qquad (7)$$

For the distribution experiments, the results of experiments at a constant acidity were fit with respect to $[X^{2-}]$ individually using either a quadratic or cubic equation to determine conditional stability quotients (α) (indicating 1:1, 1:2 and 1:3 M:L stoichiometries are appropriate). The approximate acid dependence of the conditional stability quotients was determined by plots of $\log \alpha$ versus $\log[H^+]$. An example of such a plot is given in Fig. 2 for the europium–VDPA results. These results were used to derive the appropriate relationships for the ultimate fitting of the combined data sets. Slopes of the $\log \alpha$–$\log[H^+]$ plots for all the systems investigated are given in Table 3.

The experimental results at the 4–6 acidities investigated were combined into a master table for each Eu–DPA system. The data in these master files (including [HDEHP], $[H^+]$, $[X^{2-}]$, D, weight ($1/D$)) were fit as a combined data set using the general form of eqn. (7). Forty to sixty data points were fit for each system. The model equation for the least-squares fit of the distribution data was modified to include all reasonable species, using the guidance provided by the $\log \alpha$–$\log[H^+]$ plots. An example of the agreement between experimental and calculated results is shown (for Eu–VDPA) in Fig. 3. The stability constants for the europium–diphosphonate complexes are given in Table 4.

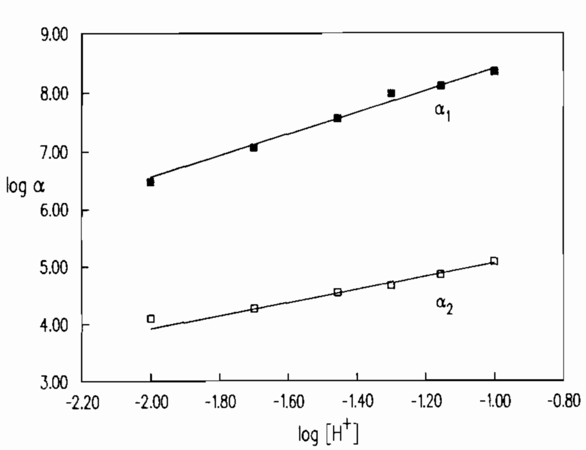


Fig. 2. Conditional stability constants (at constant acidity) log β(1 or 2) vs. $\log[H^+]$ for europium–VDPA experiments.

TABLE 3. Metal:proton stoichiometry derived from conditional stability constants

System	M:H(α_1)	M:H(α_2)	M:H(α_3)
Eu–VDPA	0.97(0.06)	1.91(0.08)	n.o.
Eu–HEDPA	0.79(0.09)	1.49(0.09)	2.30(0.21)
Eu–EDPA	0.68(0.01)	0.92(0.14)	n.o.
Eu–DHEDPA	0.35(0.05)	1.34(0.22)	n.o.
Eu–MDPA	0.63(0.12)	1.22(0.10)	n.o.

Numbers in parentheses represent 1σ uncertainty limit. n.o. = not observed.

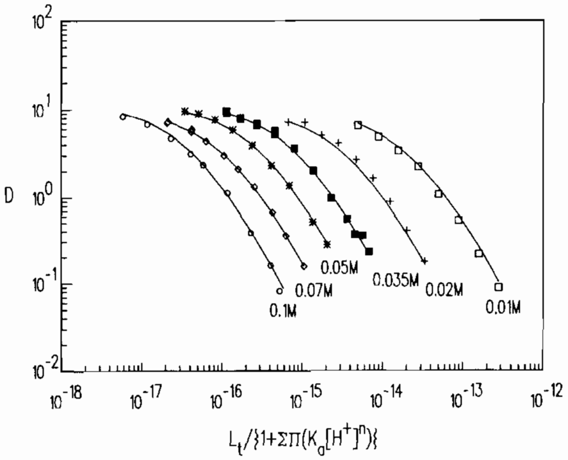


Fig. 3. Fit of europium–VDPA distribution data for the complete data set. These data are plotted as a function of $[L^{4-}]$ for visual clarity. Experimental uncertainty in the distribution ratios is less than the size of the data points. The numbers in the figure represent total acidity for each data set. Solid curves are the least-squares fits using the data in Table 4.

Discussion

Previous discussions of the protonation of aliphatic mono- and diphosphonic acids have indicated that reasonably good linear correlations of protonation constants of these species can be achieved by application of the Taft equation [26, 27]. The Taft equation relates rate or equilibrium constants, in the present case – protonation con-

TABLE 4. Stability constants for europium–DPA complexes at $T = 25$ °C, $I = 2.0$ M

β_{mhx}	$\log \beta_{mhx}$				
	Eu–HEDPA	Eu–DHEDPA	Eu–VDPA	Eu–EDPA	Eu–MDPA
β_{111}	6.43(0.01)	5.15(0.01)	5.71(0.01)	6.25(0.02)	5.99(0.01)
β_{101}	4.58(0.04)	4.11(0.02)	3.70(0.01)	4.11(0.02)	4.04(0.02)
β_{122}	11.47(0.08)	9.32(0.08)	9.96(0.01)	10.85(0.02)	10.41(0.02)
β_{112}	9.76(0.06)	n.o.	n.o.	n.o.	n.o.
β_{102}	n.o.	6.22(0.04)	6.33(0.04)	7.63(0.06)	7.11(0.04)
β_{123}	14.56(0.14)	n.o.	n.o.	n.o.	n.o.

Values in parentheses represent 2σ uncertainty limit in the respective $\log \beta_{mhx}$ values. n.o. = minor species not observed in the acid range investigated.

stants, to the inductive effect of the substituents attached to the acid group. The effect as applied to phosphonic acids has been discussed in some detail in several previous publications, to which the reader is referred for details [4, 6, 10].

Taking the 'gem-diphosphonate' group as a base, the following Taft constants are derived (using the substituent constants from Grabenstetter and Cilley [6]) for the diphosphonic acids in this report. For MDPA, two protons [$\sigma^*(\text{–H}) = 0.49$] gives $\Sigma\sigma^*(\text{MDPA}) = 0.98$; for EDPA, one proton, one methyl group ($\sigma^*(\text{–CH}_3) = 0.0$) gives $\Sigma\sigma^*(\text{EDPA}) = 0.49$; for HEDPA, one methyl group, one alpha hydroxy group ($\sigma^*(\text{–OH}) = 1.55$) gives $\Sigma\sigma^*(\text{HEDPA}) = 1.55$; for DHEDPA, one beta hydroxy group ($\sigma^*(\text{–CH}_2\text{OH}) = 0.56$), one alpha hydroxy gives $\Sigma\sigma^*(\text{DHEDPA}) = 2.11$. No directly relevant Taft constant could be found for the vinylidene group of VDPA, and in any case direct involvement of the π electron system of VDPA in the diphosphonate anion would probably negate the predictive aspect of the Taft relationship.

A plot of the $\log K_{a2-4}$ values versus $\Sigma\sigma^*$ for the diphosphonic acids in this study are shown in Fig. 4. $\log K_{a1}$ was not included in this plot because of the previous reports of Na^+–L ion pairs, which we are unable to reliably factor out. The linear correlations for the DHEDPA, EDPA and MDPA constants are: for $\log K_{a4}$ – 0.999; for $\log K_{a3}$ – 0.988; for $\log K_{a2} = 0.999$. The protonation constants for HEDPA are consistently above these linear correlation lines. A similar slight elevation is seen in the results of Grabenstetter and Cilley.

The $\log K_{a4}$ value for VDPA appears to place the relative inductive effect of the $\text{H}_2\text{C=}$ group near that for EDPA (i.e. $\Sigma\sigma^* = 0.5$–0.6). Barlin and Perrin [27] report $\Sigma\sigma^*(\text{H}_2\text{C=CH–}) = 0.56$, within the range observed for VDPA, though the groups are not strictly equivalent. Upon release of this first proton, the observed position of VDPA shifts to the $\Sigma\sigma^* = (1.4$–$1.6)$ region for the release of the second and third protons. A possible explanation for the observed shift is that the charge of the monoanion (and the higher charged anions) is delocalized over the entire molecule in VDPA. The resonance effect would result in decreased affinity of the anion for protons (increasing its acidity) relative to predictions of the Taft relationship.

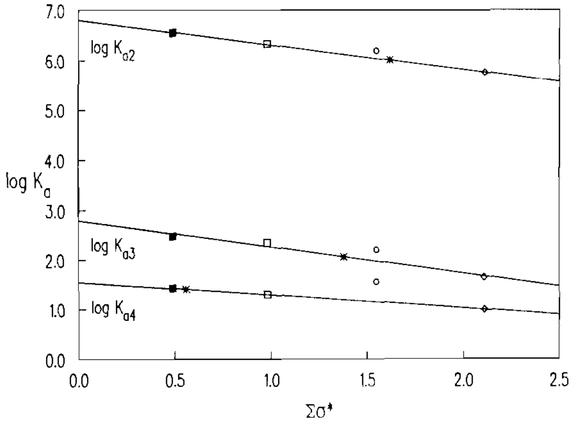


Fig. 4. DPA protonation constants as a function of $\Sigma\sigma^*$ (Taft constants): ■, EDPA; □, MDPA; ★, VDPA; ○, HEDPA; ◇, DHEDPA.

Stable carboxylic acid analogues for these compounds are unknown except for malonic acid–MDPA and methyl malonic acid–EDPA. Isomalic acid is a known analogue for HEDPA, but this compound suffers from low stability and as a result no literature values for protonation constants are available. For these analogue carboxylic acids, the trend of relative acidities is the same as that observed in the present work for the diphosphonic acids, that is, MDPA is a stronger acid than EDPA as malonic acid is stronger than methyl malonic.

Being stronger acids than corresponding carboxylic acids implies that the competition between free metal ion and proton for the free ligand species should be generally more favorable for complexation of the metal ions in the diphosphonic acids, at least in acidic solutions. Considering X^{2-} as the free ligand species for the DPAs in acidic solutions, it is instructive to compare $\log \beta_{101}$–$\log K_{a3}$ (MDPA) with

$\log \beta_1 - \log K_{a1}$ (malonic acid). The delta log value corresponds to the relative affinity of the dianion for proton versus Eu^{3+} at unit activity of each. For the present results at $I = 2.0$ M the value for MDPA is 1.69 while the corresponding value for malonic acid ($\log \beta_{101} = 3.72$, $\log K_{ai} = 5.07$ at $I = 1.0$ M, $T = 25$ °C [27]) is −1.35. The difference in the delta log values indicates that the europium–MDPA complex is three orders of magnitude stronger than the analogous dicarboxylate complex.

Extending this treatment to the other europium–diphosphonate complexes gives the relative order of stability (all data for complexes MX^+) DHEDPA (2.46) = HEDPA (2.38) > MDPA (1.69) = VDPA (1.68) = EDPA (1.63). The order is suggestive evidence for the stabilization of the metal complex by the alpha hydroxy group of HEDPA and DHEDPA, in accord with earlier reports of complexation of alkaline earth metal ions by HEDPA [9, 10]. The altered P–C–P bond angle of VDPA also appears to not adversely effect the stability of the europium complex compared to that with EDPA.

The data presented in this manuscript do not permit definitive statements regarding the nature of the metal–ligand binding in these complexes. It is conceivable that the complexes could involve species with six, five or four membered rings or possibly no chelate rings at all. With at least two protons present in each complex, they almost certainly involve a number of hydrogen bonding possibilities, intra- and intermolecular. The apparent increased stability of europium complexes with HEDPA and DHEDPA is presumably related to the presence of the alpha hydroxy group, though the present results do not otherwise support metal–ligand binding through the alcohol group.

Our practical interest in these compounds is in their application as water soluble complexants for use in liquid–liquid extraction processes. Oxalic acid is commonly used in that capacity but its use suffers from the low solubility of many of its complexes and lower effectiveness at $[H^+] < 0.01$ M. Using the thermodynamic data of this study and literature values for the protonation and europium complexation by oxalate, we can calculate the degree of lowering of an extraction coefficient. A minor modification of eqn. (7) permits calculation of a 'stripping factor' (D_o/D), a multiplicative factor by which distribution ratios are lowered when the metal ion is complexed in the aqueous phase. If the distribution ratio in the absence of the complexant is defined as D_o, the appropriate equation is (charges omitted for simplicity)

$$D_o/D = 1 + \Sigma\beta_{mhx}[H]^h[X]^x \tag{8}$$

The degree of lowering of the distribution ratio is thus proportional to the stability constant, the total ligand concentration, the acidity and the metal complex stoichiometry.

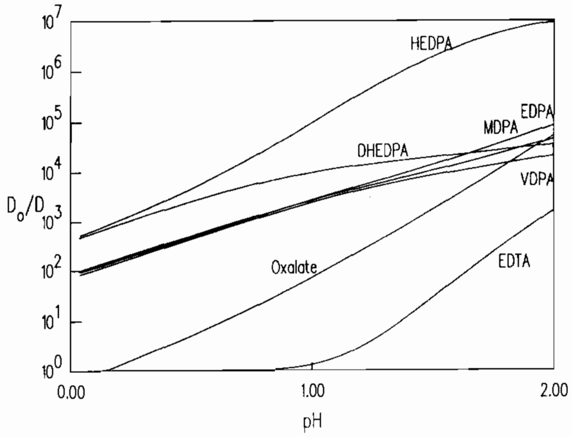


Fig. 5. Stripping factor for DPAs, oxalic acid and EDTA at 0.2 M total complexant concentration and pH 0–2.

At 0.2 M total ligand concentration, the diphosphonic acids are clearly superior complexants for europium, as the calculated results in Fig. 5 indicate. In the most acidic solutions, oxalic acid has minimal effect on the distribution ratio of europium while the diphosphonic acids lower D_{eu} by a factor of at least 100. At pH 2 the complexation advantage of the most of the diphosphonic acids has been lost except for HEDPA. The stripping factor for europium by HEDPA remains nearly three orders of magnitude greater than that by oxalic acid even at pH 2, largely because europium speciation in 0.2 M HEDPA under these conditions is dominated by the 1:3 metal to ligand complex $EuH_2X_3^-$. The relative ineffectiveness of EDTA as complexant in acidic solution is also shown in this figure.

Preliminary observations indicate that these complexants perform admirably in the function for which they were designed, that is, as stripping/holdback reagents for polyvalent metal ions (as represented by europium) in solvent extraction separation schemes. The thermodynamic parameters presented here predict europium stripping factors reasonably well even in solutions of acidities greater than those used in this study. The solubility of europium–DPA complexes also appears to exceed that of the corresponding oxalates. These aspects of metal complexation by substituted methane diphosphonic acids are under investigation and a manuscript outlining applications of these ligands is forthcoming.

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References

1 A. E. Martell and R. M. Smith, *Critical Stability Constants,* Vols. 1–5, Plenum, New York, 1977.

2 *IUPAC Stability Constants of Metal Ion Complexes, Part A, Inorganic Ligands, Part B, Organic Ligands,* Pergamon, Oxford, 1979.

3 A. P. Toste and R. B. Myers, *The Effects of Natural Organic Compounds and of Microorganisms on Radionuclide Transport, Proc. NEA Workshop, Paris, France, June 12, 1985,* p. 57, and refs. therein.

4 R. L. Carroll and R. R. Irani, *Inorg. Chem., 6* (1967) 1994.

5 R. R. Irani and K. Moedritzer, *J. Phys. Chem., 66* (1962) 1349.

6 R. J. Grabenstetter and W. A. Cilley, *J. Phys. Chem., 75* (1971) 676.

7 H. Wada and Q. Fernando, *Anal. Chem., 43* (1971) 751.

8 M. I. Kabachnik, R. P. Lastovskii, T. Ya. Medved', V. V. Medyntsev, I. D. Kolpakova and N. M. Dyatlova, *Dokl. Akad. Nauk SSSR, 177* (1967) 582.

9 H. Wada and Q. Fernando, *Anal. Chem., 44* (1972) 1640.

10 R. L. Carroll and R. R. Irani, *J. Inorg. Nucl. Chem., 30* (1968) 2971.

11 B. D. Mulkina, S. I. Zhdanov and E. A. Mambetkaziev, *Russ. J. Gen. Chem., 48* (1978) 22.

12 K. B. Yatsimirskii, M. I. Kabachnik, M. A. Konstantinovskaya, E. I. Sinyavskaya, T. Ya. Medved' and N. P. Nesterova, *Russ. J. Inorg. Chem., 22* (1977) 435.

13 T. A. Chernova and K. V. Astakhov, *Zh. Fiz. Khim., 45* (1971) 1114.

14 Sh. E. Vassershtein and N. V. Nam, *Zh. Neorg. Khim., 18* (1973) 1028.

15 *Merck Index,* Merck & Co., Inc., Rahway, NJ, 10th edn., 1983, entry 3812, p. 557.

16 A. A. Elesin, A. A. Zaitsev, N. A. Ivanovich, V. A. Karaseva and G. M. Yakovlev, *Radiokhimiya, 14* (1972) 546.

17 A. A. Elesin, A. A. Zaitsev, S. S. Kazakova and G. N. Yakovlev, *Radiokhimiya, 14* (1972) 541.

18 R. C. Gatrone, *J. Org. Chem., 54* (1989) 4272.

19 G. R. Choppin, D. A. Kelly and H. E. Ward, in D. Dyrssen, J. O. Liljenzin and J. Rydberg (eds.), *Solvent Extraction Chemistry,* North Holland, Amsterdam, 1967, p. 46.

20 J. J. Schubert, *J. Phys. Coll. Chem., 52* (1948) 340.

21 H. M. Irving and H. S. Rossotti, *J. Chem. Soc.,* (1954) 2904.

22 K. L. Nash and J. M. Cleveland, *Radiochim. Acta, 36* (1984) 129.

23 A. E. Martell and R. M. Smith, *Critical Stability Constants,* Vols. 3 and 4, Plenum, New York, 1977, p. 92; p. 56, 59.

24 L. Zikovsky, *J. Inorg. Nucl. Chem., 35* (1973) 2917.

25 M. S. Caceci and G. R. Choppin, *Radiochim. Acta, 33* (1983) 101.

26 R. W. Taft, Jr., *J. Chem. Phys., 26* (1957) 93.

27 G. B. Barlin and D. D. Perrin, *Q. Rev. (London),* (1966) 75.