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Stability Constants of Europium Complexes with a Nitrogen Heterocycle Substituted Methane-1,1-diphosphonic Acid

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Abstract

Even in moderately acidic solutions ($[H^+] > 0.01$ M), N-piperidinomethane-1,1-diphosphonic acid (H_4PMDPA) is a strong complexant of trivalent lanthanide ions that shows enhanced complex solubility over previously studied 1,1-diphosphonic acids. The protonation constants of PMDPA in 2.0 M H/$NaClO_4$ were determined by potentiometric and NMR titrations, and the stability constants for the formation of complexes with Eu^{3+} were determined by solvent extraction. The difference in protonation equilibria induced by the addition of the nitrogen heterocycle results in an increase in the complexation strength of PMDPA. In solutions containing 0.1 M H^+ and ligand concentrations greater than 0.02 M, PMDPA is the most effective 1,1-diphosphonic acid for europium complexation studied thus far.

Keywords: Europium, Phosphonic acids, Stability constants, Protonation constants, Solvent extraction

1. Introduction

Recent studies of f-element complexation by methane-1,1-diphosphonic acids (DPAs) have demonstrated the superiority of these ligands over conventional carboxylic or aminopolycarboxylic acid ligands in several areas of lanthanide and actinide separations [1-6]. The most notable improvement over their carboxylic acid counterparts is the controllable instability of DPAs. At elevated temperatures, or in the presence of mild oxidants, they decompose *in situ* to the simple chemical species H_3PO_4, CO_2, and H_2O. Carboxylic acid based ligands, on the other hand, are remarkably persistent, a feature which increases

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the difficulty of storing or controlling the migration of escaped radioactive wastes [7]. Moreover, in the acidic solutions ($[H^-] > 0.01$ M) usually encountered in processing f-element cations, DPAs form stronger, more soluble complexes then their organic acid siblings.

While DPAs are more soluble ligands that form more soluble complexes in acidic solutions than common carboxylic acids, the solubilities of the f-element - DPA complexes studied thus far are limited to approximately millimolar concentrations in less acidic solutions. Consequently, we have begun to explore the f-element complexation chemistry of the nitrogen heterocycle substituted methane diphosphonic acids, N-morpholinomethane-1,1-diphosphonic acid and N-piperdinomethane-1,1-diphosphonic acid, which reportedly form more soluble Fe^{3+} complexes than other aminomethane-1,1-diphosphonic acids [8]. Although our molecular mechanics calculations suggest that the nitrogen atom in PMDPA is not properly oriented to coordinate metal ions bound to the phosphonate groups, the introduction of the amine functionality should alter the protonation and metal complexation equilibria as compared to the previously studied DPAs. To investigate this, we have studied the protonation equilibria of N-piperdinomethane-1,1-diphosphonic acid (H_4PMDPA) by potentiometric and NMR titrations, and its Eu^{3+} complexation equilibria by tracer scale solvent extraction between p[H] 1.0 and 2.0.

2. Experimental details

H_4PMDPA was prepared by reacting 1-formylpiperidine with phosphorous trichloride and phosphorous acid, after the method used by Rusina *et al.* [9]. It was purified by precipitation from H_2O and analyzed by ^{31}P NMR spectroscopy and titration with NaOH in H_2O without supporting electrolyte. Sodium perchlorate monohydrate was recrystallized at least three times from H_2O and filtered through a 1.0 μm membrane until the total iron concentration of a 2.0 M solution was less than 2×10^{-6} M. Extraction studies were carried out using bis(2-ethylhexyl)phosphoric acid (HDEHP) purified by the method of Peppard *et al.* [10] in Photrex grade toluene (J. T. Baker). The p[H] (p[H] = -log H^+ concentration in molarity) was measured with an Orion Ross combination glass electrode calibrated by $HClO_4$/NaOH titrations in 2 M $NaClO_4$ at 25.0 °C.

The protonation constants of PMDPA were determined, where possible, by potentiometric titration of 0.0025 M H_4PMDPA with NaOH in 2.0 M $NaClO_4$ at 25.0 °C under N_2. The constants for the protonation of H_3PMDPA^- and H_4PMDPA were also determined from the ^{31}P NMR chemical shifts of 10% D_2O solutions containing 0.01 M H_4PMDPA in 2.0 M H/$NaClO_4$ measured between p[H] 1.1 and 4.8. Decoupled spectra were collected on a 300 MHz GE Omega spectrometer at 25 °C with 85% H_3PO_4 as an external standard.

The stability constants of Eu$(H_hPMDPA)_n$ complexes were measured by solvent extraction using a radiochemically pure $^{152,154,155}Eu^{3+}$ tracer in 0.01 M HNO_3 obtained from laboratory stocks. Equal volumes of a pre-equilibrated HDEHP containing toluene phase, and an aqueous phase containing 2×10^4 cpm Eu^{3+} and 0-0.05 M H_4PMDPA at $I = 2.0$ M in glass culture tubes were contacted by rotary mixing for 3 hours at room temperature, with intermittent vortex mixing over a final hour as the tubes came to equilibrium at 25.0 °C. An aliquot was taken from each phase for γ-counting to determine the europium distribution ratio, expressed as the ratio of the total europium concentration in the organic phase to the total europium concentration in the aqueous phase. The HDEHP concentration and the total PMDPA concentration spanned at each p[H] were chosen to maintain the values of the distribution coefficients between 0.01 and 100 as much as possible.

3. Results

The protonation constants of PMDPA were determined by iteratively fitting both the potentiometric (Figure 1) and NMR (Figure 2) titration data. The potentiometric data was fit using the program LETAGROP ETITR [11], while the chemical shift data was fit, using the Marquardt-Levenberg non-linear least squares algorithm as implemented by the program Origin, to the equation

$$\delta_T = \frac{\sum_{h=0}^{3} \delta_{(h+2)} \beta^{prot}_{(h+2)} [H^+]^h}{\sum_{h=0}^{3} \beta^{prot}_{(h+2)} [H^+]^h} \qquad (1)$$

where δ_T is the measured ^{31}P NMR chemical shift, $\delta_{(h+2)}$ is the chemical shift of $H_{(h+2)}PMDPA^{(h-2)}$, and

$$\beta^{prot}_{(h+2)} = \frac{[H_{(h+2)}PMDPA^{(h-2)}]}{[H_2PMDPA^{2-}][H^+]^h} \tag{2}$$

In the NMR titration, the hydrogen ion concentration was known from the p[H] measurements, and β_3^{prot} was measured by the potentiometric titration. In both the NMR and extraction experiments, H_2PMDPA^{2-} was chosen as the base ligand rather than $PMDPA^{4-}$ since the less protonated PMDPA species constitute less than 0.1% of the total uncomplexed ligand over the p[H] range studied in those experiments. Beginning with an estimated β_3^{prot}, the protonation constants derived from fitting one titration experiment were used to fit the data from the other experiment. This process continued until constant values were obtained. The results of the fitting, including the uncertainties at $\pm 2\sigma$, are summarized in Table 1.

Preliminary examination of the extraction data indicated that complexes containing 1, 2, and 3 equivalents of PMDPA form in the conditions studied. Thus the europium extraction data was used to obtain apparent stability constants at each p[H] for the reaction

$$Eu^{3+} + n\ H_2PMDPA^{2-} \rightleftharpoons Eu(H_2PMDPA)_n^{3-2n} \tag{3}$$

where $n = 1, 2,$ or 3, assuming that only mononuclear complexes are formed, that no Eu-PMDPA complexes are extracted into the organic phase, and that ClO_4^- is a non-complexing anion. The average H^+ stoichiometry for each value of n was deduced from the slope of log-log graphs of the apparent stability constants against the H^+ concentration [1-3]. As summarized in Figure 3 and Table 2, the full set of distribution ratios, including those measured in the absence of PMDPA, were fit to the expression

$$\frac{D_o}{D} - 1 = \sum_{n=1}^{3} \sum_{h=0}^{2n} \beta_{hn} [H^+]^h [H_2PMDPA^{2-}]^n \tag{4}$$

where D_o is the distribution coefficient calculated for each HDEHP and H^+ concentration using the experimentally determined extraction constant, ($K_{ex} = 0.239 \pm 0.006$), and the dependency of the distribution coefficient on the HDEHP and H^+ concentrations. The non-linear least squares fit of the distribution data was weighted to account for pipetting and radioactive counting errors and the uncertainty in the extraction constant. All values of n and h consistent with the average H^+ and H_2PMDPA^{2-} stoichiometries derived from the conditional stability constants of equation 3 were considered in the model selection process. Corrections to the H_2PMDPA^{2-} concentrations for the amount of ligand present in Eu complexes were not necessary since the total ligand concentration was always at least five orders of magnitude greater than the Eu concentration.

4. Discussion

As expected, introduction of the amine functionality results in increased solubility for the Eu-PMDPA complexes over other Eu-DPA complexes, and alters the protonation equilibria of the diphosphonic acid fragment, shifting all the phosphonate equilibria to lower pK_a values. It should be noted that the constants calculated for the acid equilibria are not corrected for Na^+ ion pairing with the phosphonate groups at higher p[H] [12-14]. These ion pairing equilibria are apparent in the potentiometric data (Figure 1) where the third equivalence point is displaced from the theoretical value and the fit to the data at high p[H] is poor. However, attempts to include the effect of Na^+ species while modeling the potentiometric data were not successful, presumably due to the constant, large excess of sodium present.

The ^{31}P NMR chemical shifts demonstrate the absence of ion pairing below p[H] 5, and also argue against a previously suggested PMDPA protonation sequence. Sodium-phosphonate ion pairing and nitrogen deprotonation each cause the phosphorous resonances of aminomethylphosphonates to shift downfield by several ppm [15,16]. In contrast, the H_3PMDPA^- and H_2PMDPA^{2-} chemical shifts (Table 1) differ by less than 1 ppm, too little to indicate either ion pairing or nitrogen protonation equilibria for either species. This result also refutes the theoretical suggestion that protonation of the piperdino nitrogen in PMDPA occurs with $pK_a = 4.6$ [8]. Calorimetric measurements show that the protonation of $PMDPA^{4-}$ is quite exothermic, -55 kJ/mol, while the other $H_hPMDPA^{(h-4)}$ protonation equilibria are only slightly endo- or exothermic [17]. Furthermore, the enthalpy of the first protonation compares favorably with literature reports for the protonation of piperidine (-55.1 kJ/mol at $I = 0.5$ M) [18]. Combined with the observation that the protonation of phosphonate oxygens is primarily entropy driven with a smaller (0 ± 15 kJ/mol) enthalpy contribution [19], these results imply that the piperdino nitrogen is protonated first (at high p[H]).

Compared to other DPAs that do not contain amino groups, the phosphonate protonation equilibria of PMDPA occur at pK_a values 1-2 log units lower, except for $pK_{a,2}$, (corresponding to the equilibrium between $R\text{-}C(PO_3H^-)_2$ and $R\text{-}C(PO_3H_2)(PO_3H^-)$), which is 2.0 ± 0.5 for all the DPA ligands we have studied [1]. Consequently, the phosphonate groups of PMDPA retain a significant partial negative charge as zwitterions at p[H] values where DPAs without the amino functionality are fully protonated. This should allow PMDPA to complex a greater fraction of metal ions at low p[H].

The stability constants and stoichiometries of the complexes formed between Eu^{3+} and H_2PMDPA^{2-} from p[H] 1 to 2 derived from the solvent extraction experiments (Table 2) are similar to the complexes of Eu^{3+} with other DPAs if only the degree of protonation of the phosphonate groups is considered [1]. The previously reported complex stoichiometries for the reaction

$$m\ Eu^{3+} + h\ H^+ + n\ H_2DPA^{2-} \rightleftharpoons Eu_mH_h(H_2DPA)_n^{3m-h-2n} \qquad (5)$$

involve 101, 111, 102, and 122 (mhn) complexes between p[H] 1 and 2, with the exception of 1-hydroxy ethane-1,1-diphosphonic acid (HEDPA) which is best described by 101, 111, 102, 112, and 123 complexes. As illustrated in Figure 4, direct comparison of the stoichiometries of the Eu-PMDPA complexes with those of other DPAs based on the degree of protonation of the phosphonate groups (i.e. ignoring protonation of the piperdine), requires the Eu^{3+}:H^+:H_2PMDPA^{2-} stoichiometries reported in Table 2 to be adjusted to express the stoichiometry based on H_3PMDPA^-. When this is done, the best model for Eu-PMDPA complexation corresponds to the 101, 111, 102, 122, and 123 complexes of other DPAs. The formation of the 123 complex between Eu and PMDPA is unusual, as it was only observed in the Eu-HEDPA complexes previously [1].

Calculations of the fraction of Eu^{3+} that is not complexed by a series of methane-1,1-diphosphonic acids are depicted in Figure 5. As the H^+ or total ligand concentration is lowered, Eu^{3+} complexation by PMDPA is similar to that of the simplest DPA, methane-1,1-diphosphonic acid. Near p[H] = 1, where the difference in the protonation of PMDPA and the other DPAs is pronounced, $EuH_2(H_3PMDPA)_3^{2+}$ becomes the dominant complex when the total PMDPA concentration exceeds ca. 0.01 M. Under these conditions, PMDPA becomes a more effective ligand than HEDPA, the strongest ligand of the DPAs studied thus far. The $EuH_2(H_2HEDPA)_3^-$ complex dominates its speciation near p[H] = 2, where HEDPA is most effective. The corresponding ability of PMDPA to form the 123 complex at lower p[H] arises from its very low $pK_{a,1}$

value which allows a larger fraction of the PMDPA molecules to retain a negative charge on the phosphonate groups in 0.1 M acid. Thus, the protonation of the piperdino nitrogen, which is responsible for a general decrease in the pK_a values of the four phosphonate protonation equilibria and the formation of a zwitterion in the neutral H_4PMDPA species, allows the formation of the strong complex, $EuH_2(H_3PMDPA)_3^{2+}$, under acidic conditions of moderate ligand concentrations. This complex makes PMDPA the most effective DPA for the complexation of trivalent lanthanides in acidic solutions we have studied.

While the availability of H_3PMDPA^- and H_4PMDPA to form the 123 complex is obviously tied to the protonation constants of the ligand, the strength of lanthanide-DPA complexes appears due to hydrogen bonding within and around the complexes. As discussed previously, solution calorimetric and Eu fluorescence measurements of a number of Eu-DPA complexes suggest that the greater strength of Eu-HEDPA complexes, compared to the other Eu-DPA complexes, cannot be attributed to direct Eu coordination by the α-hydroxy group of HEDPA [19]. When coordinated to a lanthanide cation in solution, the phosphonate groups of DPAs form an unusually ordered network of hydrogen bonds between ligands within a molecule of the complex and between the coordinated ligands and second sphere water molecules (relative to the lanthanide cation). In the HEDPA complexes studied, the α-hydroxy group also is involved in the formation of the H-bonding network, as reflected in a somewhat more exothermic (4-7 kJ/mol) complexation enthalpy. Like the α-hydroxy group of HEDPA, the protonated amine group of PMDPA provides a site for hydrogen bonding not present in the other DPAs studied. If this is indeed the case, it should be manifested in the yet unmeasured enthalpy of complex formation between Eu^{3+} and PMDPA.

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Figure 1. Potentiometric titration data (□) and LETAGROP fit (—) for the titration of 2.40×10^{-3} M H_4PMDPA with 0.1 M NaOH at I = 2 M and 25.0 °C.

Figure 2. ^{31}P NMR chemical shifts of 0.01 M PMDPA in 2 M $H/NaClO_4$ at 25 °C. (□) experimental data, (—) fit.

Figure 3. Extraction of Eu^{3+} by bis(2-ethylhexyl)phosphoric acid in toluene as a function of the H_2PMDPA^{2-} concentration in 2M $H/NaClO_4$ at 25 °C. Lines are the fit of the data to the model.

Figure 4. A comparison of diprotonated 1-hydroxyethane-1,1-diphosphonic acid, $H_2(HEDPA^{2-})$, and triprotonated N-piperdinomethane-1,1-diphosphonic acid, H_3PMDPA^-.

Figure 5. *Concentration of* Eu^{3+} *not complexed by methane-1,1-diphosphonic acids* at A) p[H] = 1 with varying ligand concentration and B) 0.025 M ligand with varying p[H]. (—) 1-hydroxyethane-1,1-diphosphonic acid, (--) methane-1,1-diphosphonic acid, and (···) N-piperdinomethane-1,1-diphosphonic acid.

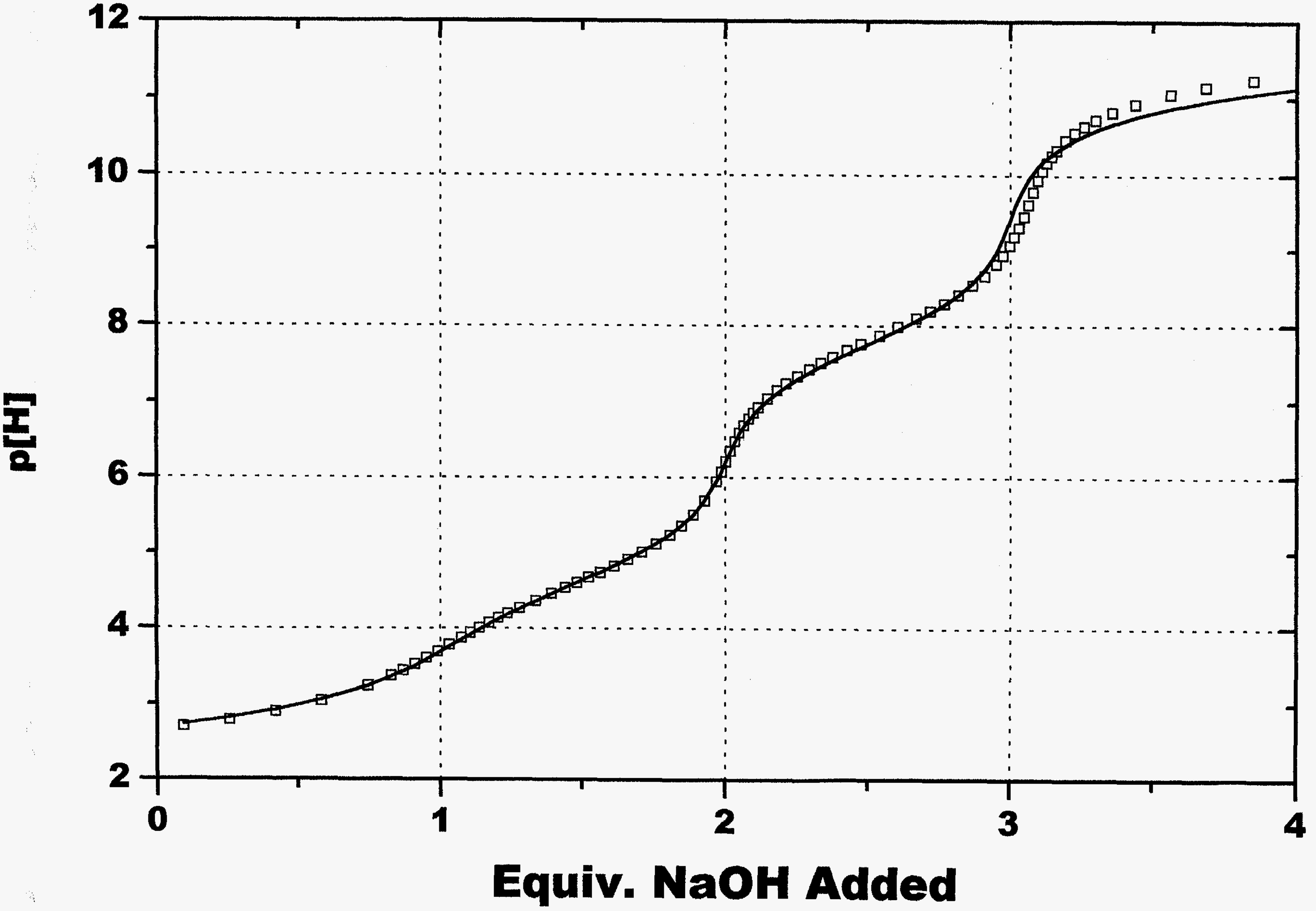
Species	Method used[a]	pK_a	^{31}P NMR Chemical Shift (ppm)
H_5PMDPA^+	NMR	0.3 ± 0.1	9.37 ± 0.92
H_4PMDPA	NMR, pot.	2.02 ± 0.02	7.45 ± 0.01
H_3PMDPA^-	pot.	4.62 ± 0.01	7.391 ± 0.004
H_2PMDPA^{2-}	pot.	7.76 ± 0.03	7.98 ± 0.01
$HPMDPA^{3-}$	pot.	11.5 ± 0.1	

[a] pot. = potentiometry

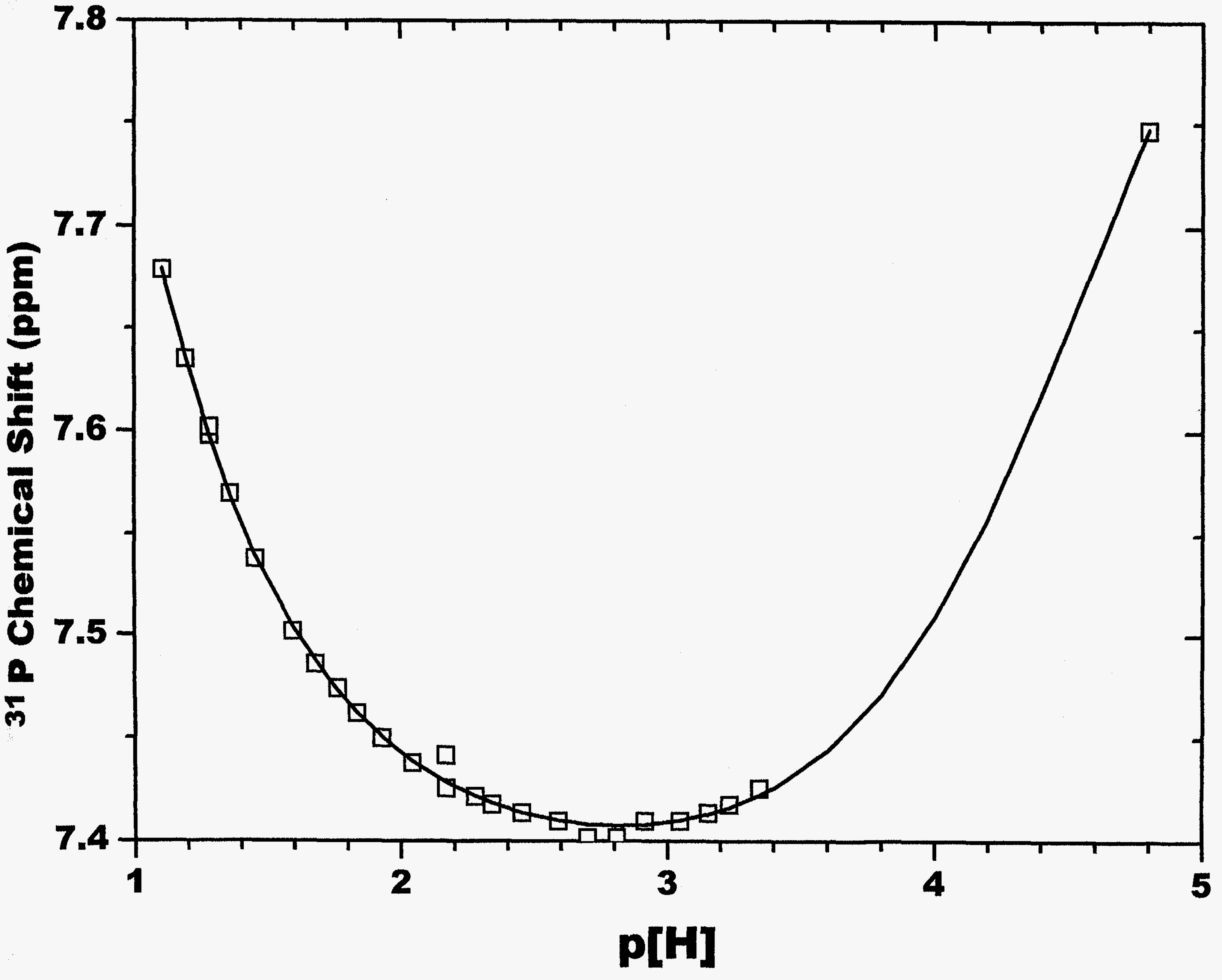
Table 1. Acid dissociation constants and chemical shifts of PMDPA at 25 °C and I = 2 M $NaClO_4$ with uncertainties reported at ±2σ.

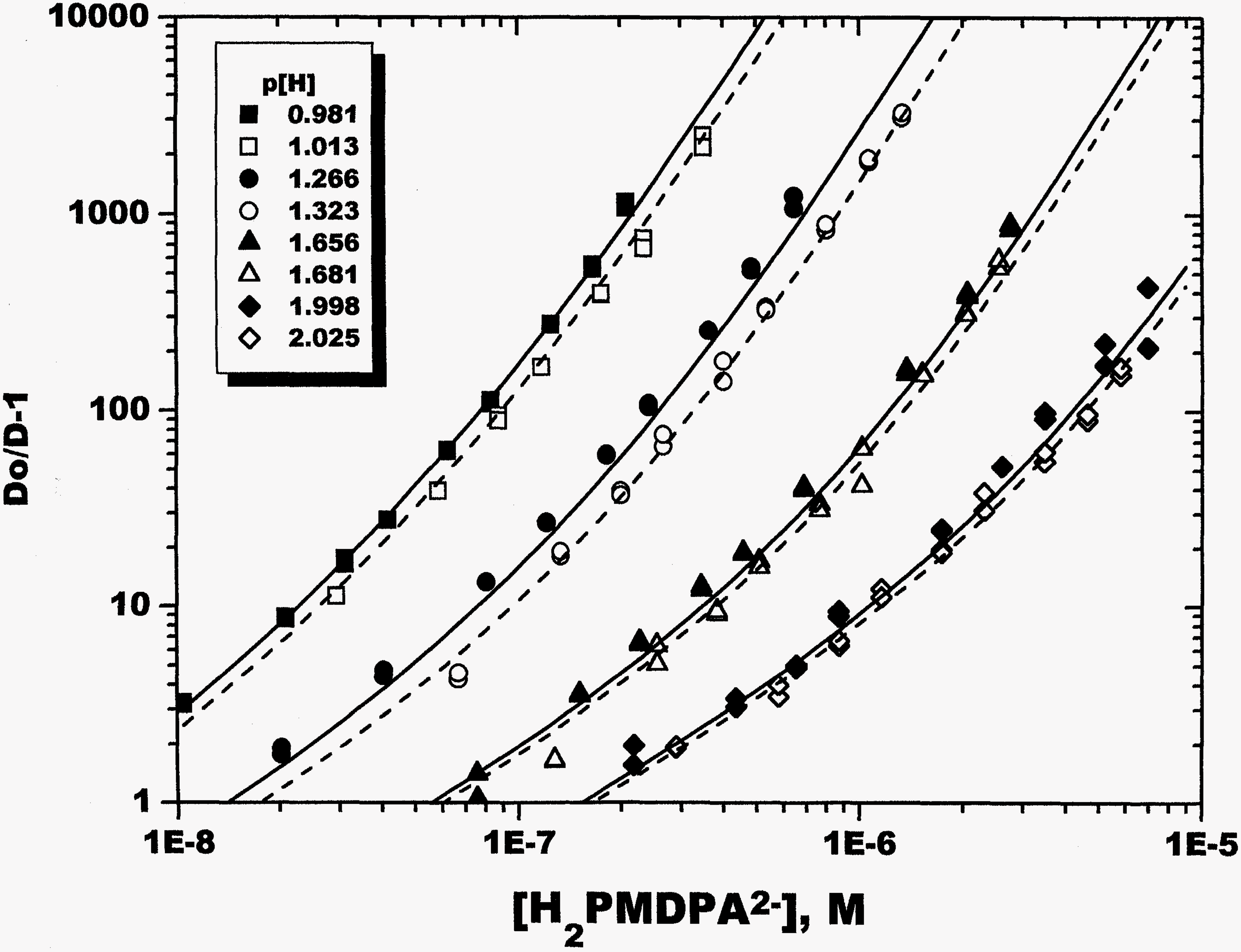
	Nitrogen Adjusted	
Species, mhn	Species, m(h-n)n	log β_{mhn}
111	101	8.70 ± 0.08
121	111	10.04 ± 0.20
122	102	16.24 ± 0.12
142	122	19.94 ± 0.08
153	123	27.57 ± 0.08

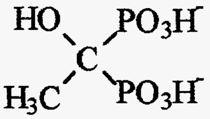
Table 2. Europium-H_2PMDPA^{2-} stability constants measured at 25 °C and $I = 2$ M $NaClO_4$ with uncertainties at $\pm 2\sigma$.



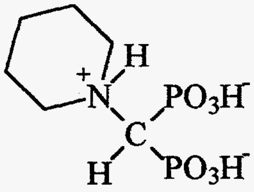
12
10
8
6
4
2
p[H]
0
1
2
3
4
Equiv. NaOH Added


7.8
7.7
7.6
7.5
7.4
31 P Chemical Shift (ppm)
1
2
3
4
5
p[H]

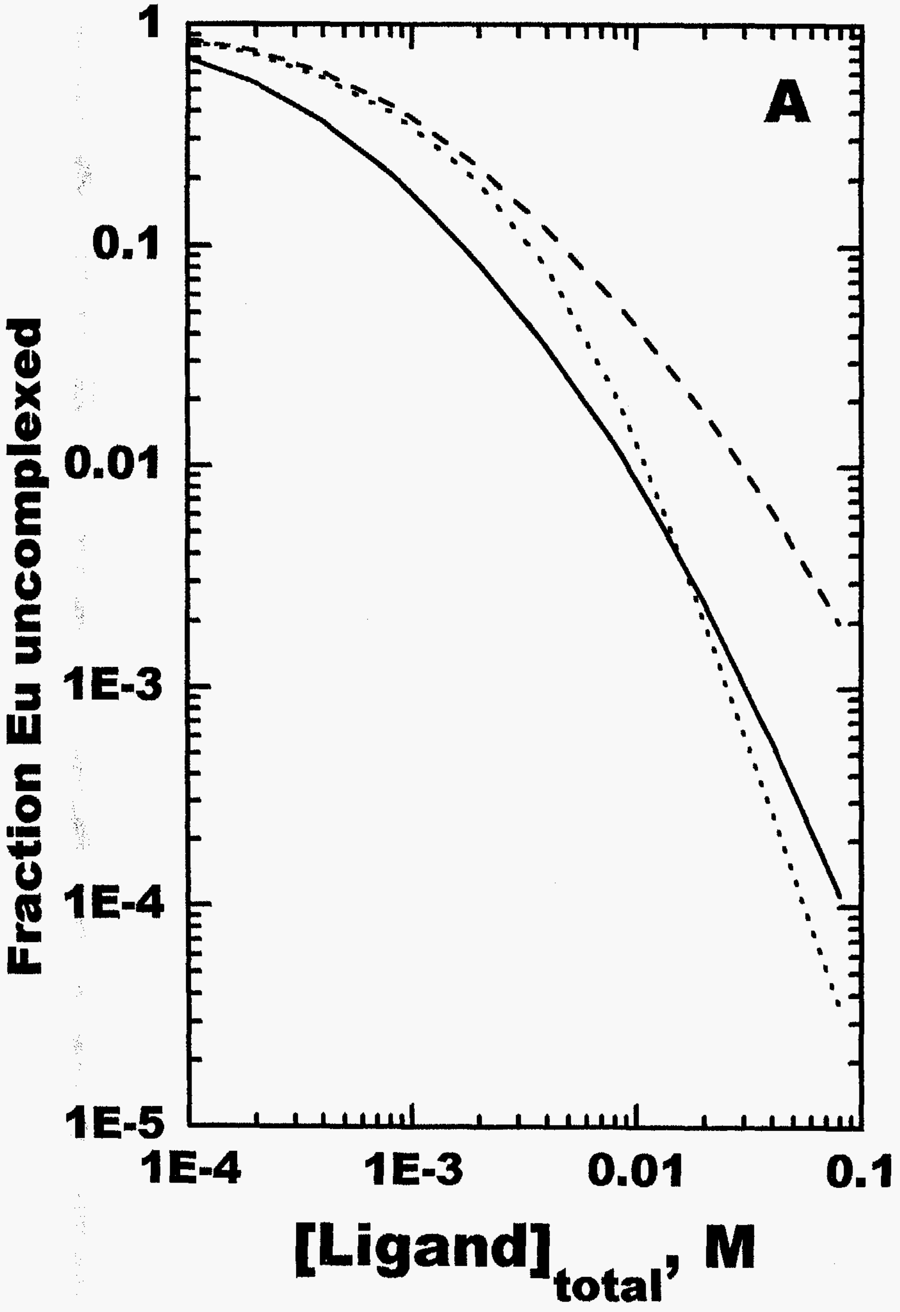

p[H]
■ 0.981
□ 1.013
● 1.266
○ 1.323
▲ 1.656
△ 1.681
◆ 1.998
◇ 2.025
10000
1000
100
10
1
Do/D-1
1E-8
1E-7
1E-6
1E-5
$[H_2PMDPA^{2-}]$, M

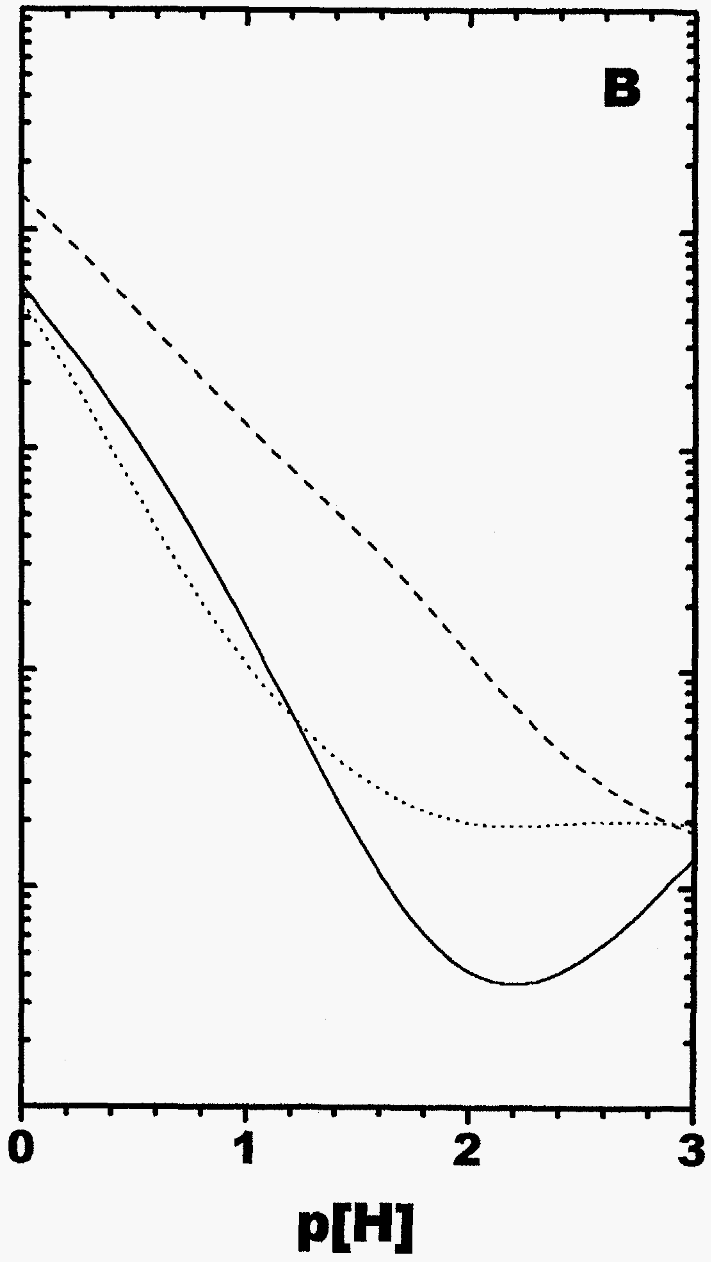


$H_2(HEDPA)^{2-}$



$H_3(PMDPA)^{-}$


A
Fraction Eu uncomplexed
1
0.1
0.01
1E-3
1E-4
1E-5
1E-4
1E-3
0.01
0.1
[Ligand]$_{total}$, M


B
0
1
2
3
p[H]