CONF-950946--7

SAND95-2005C

COMPLEXATION STUDY OF NpO_2^+ AND UO_2^{2+} IONS WITH SEVERAL ORGANIC LIGANDS IN AQUEOUS SOLUTIONS OF HIGH IONIC STRENGTH

Marian Borkowski[*], Stefan Lis[**] and G. R. Choppin

Department of Chemistry, Florida State University, Tallahassee, FL 32306-3006, USA
On leave: [*]Institute of Nuclear Chemistry and Technology, 03-195 Warsaw, Poland
[**] Faculty of Chemistry, Adam Mickiewicz University, 60-780 Poznan, Poland

ABSTRACT

The acid dissociation constants, pK_a, and the stability constants for NpO_2^+ and UO_2^{2+} have been measured for certain organic ligands [acetate, α-hydroxyisobutyrate, lactate, ascorbate, oxalate, citrate, EDTA, 8-hydroxyquinoline, 1,10-phenanthroline, and thenoyltrifluoroacetone] in 5 m (NaCl) ionic strength solution . The pK_a values were determined by potentiometry or spectrometry. These methods, as well as solvent extraction with ^{233}U and ^{237}Np radiotracers, were used to measure the stability constants of the 1:1 and 1:2 complexes of dioxo cations. These constants were used to estimate the concentrations required to result in 10 % competition with hydrolysis in the 5 m NaCl solution. Such estimates are of value in assessing the solubility from radioactive waste of AnO_2^+ and AnO_2^{2+} in brine solutions in contact with nuclear waste in a salt-bed repository.

Key words: *Neptunyl/ Uranyl/ Complexes/AcidConstants/Stability Constants*

INTRODUCTION

Deep geologic repositories are under development in a number of countries for permanent disposal of nuclear waste. Subsurface salt beds in remote areas have a number of advantages as repositories for nuclear wastes. In the United States, the Waste Isolation Pilot Plant (WIPP) is such a planned repository. Disposal of radioactive waste in salt bed repositories requires modeling metal speciation in solutions of high ionic strengths to estimate the potential rate of migration of radionuclides should they be released from the wastes. Migration depends on the time required for brines to flow from the repository to the accessible environment (hydrology) and on the way in which the radionuclides might interact with the waste brines and geologic mediia (chemistry). The latter can be affected by the extent to which the radionuclides can interact with anionic ligands from the wastes that dissolve in the brine solutions. For actinide speciation, little data are available for the complexation with such ligands above 2 m ionic strength.

It is generally assumed that a transuranic ion would equilibrate with an inorganic and organic ligand in the brine to the extent measured by the stability constant. Complexation would be influenced by factors such as the temperature and ionic composition of the brine solutions.

For the complexation reaction in solution,

$$M + nL \longleftrightarrow M L_n \qquad (1)$$

a "concentration" stability constant, β_n, can be expressed in a particular ionic medium by

$$\beta_n = [M L_n]/[M][L]^n \qquad (2)$$

In this work, we report the values of log β_n in I = 5.0 m (NaCl) ionic strength solution and the pKa of some organic anions in the same solution. The organic ligands are those likely to be present in the wastes considered for disposal in the WIPP repository.

EXPERIMENTAL

Chemicals:

Analytical grade sodium chloride, acetic, citric, oxalic, lactic, α-hydroxyisobutyric, and ascorbic acids, EDTA, 1,10-phenanthroline (phen), and 8-hydroxyquinoline (oxine) were used with no additional purification. Thenoyltrifluoroacetone (TTA), was purified by a vacuum sublimation at 44-45^{0}C. Reagent grade hydrochloric acid and sodium hydroxide (Fisher, Certified A.C.S.) were used as received. Distilled, deionized water (E-Pure, Barnstead) was used in all experiments for aqueous solutions. Di(2-ethylhexyl)phosphoric acid, HDEHP, (minimum 95%) was obtained from Sigma and purified according to McDowell et al.[1]. The organic extractant solutions were prepared in n-heptane of 6×10^{-6} M HDEHP for uranyl ion and 2×10^{-2} M for neptunyl ion. The ^{233}U and ^{237}Np tracers were obtained from Oak Ridge National Laboratory.

Instrumentation:

A Tri-Carb 4000 liquid scintillation counter (Packard) was used in this work with EcoLume (ICN) as the liquid scintillation cocktail (40% capacity for high ionic strength solution). The counting time for each sample was 10 minutes.

Glass scintillation vials used in the extractions were silanized by the method of Caceci and Choppin [2] to minimize loss of tracer by sorption to the walls in neutral solutions.

An automatic titration system, consisting of a Schott Gerate burette and IBM computer was used for potentiometric titrations and data collecting. The pH measurements were made with a Corning combination glass electrode standardized to pcH (- log [H^+], molarity) by a strong acid/strong base titration at 5.0 m (NaCl) ionic strength.

All UV, VIS and IR spectra were obtained with a Cary-14 spectrophotometer (OLIS upgraded). Digitally stored spectra were processed using the Quattro-Pro for Windows program on an IBM compatible 80486 PC.

Radiotracers ^{233}U and ^{237}Np were purified with the use of ion exchange technique and checked for purity by alpha spectrometry (ORTEC). No detectable impurities were present in the U and Np samples. ^{233}Pa, the active daughter of ^{237}Np, was removed from tracer ^{237}Np solution by extraction with HDEHP prior the extraction experiments.

An ionic strength of 5.0 m was maintained by addition of weighed amounts of solid NaCl. All NaCl solutions were filtered through a Nalgene Disposable Filter (0.2 μm pore size).

Procedures:

Determination of pK_a values

The pKa values of acetic, α-hydroxyisobutyric, ascorbic, lactic, oxalic, citric acids and EDTA were determined at I=5.0 m (NaCl) ionic strengths by titration of a 0.01 M solution of organic acid (0.005 M of oxalic and 0.0025 M of citric acids) in 5.0 m (NaCl) solution with 0.01 M NaOH in 5.0 m (NaCl) solution. For TTA, the ligand protonation constant cannot be determined by titration with strong base because of interfering cleavage of the hydrate to the trifluoroacetonate ion [3] so titration by strong acid was used. The potentiometric titration of EDTA was performed as follows: the solution of 0.001 M Na_2EDTA and 0.002 M HCl in 5.0 m (NaCl) solution were titrated with 0.01 M NaOH in 5.0 m (NaCl) solution.

The pK_a values of oxine and 1,10-phenahthroline, at I=5.0m (NaCl) ionic strength, were obtained by spectrometric measurement of the changes in absorptivities at different pcH values.

Solvent extraction procedure

The extraction procedure was based on the previously described procedures [4,5]. Tracer solutions were prepared such that 10 microliters of ^{233}U and ^{237}Np had an activity of ~30000 cpm, which, when added to 5 mL of aqueous phase, produced a solution ~1×10^{-7} M of ^{233}U and ~1×10^{-6} M ^{237}Np. Five mL of 6×10^{-6} or 2×10^{-2} molar HDEHP in heptane was added to the vials with the 5 mL aqueous phase I=5.0 m (NaCl + organics), and the mixture agitated on a mechanical shaker at 25°C for one hour. After shaking, the vials were centrifuged for five minutes, after which 1.00 mL duplicates of the aqueous and organic phases were transferred into plastic scintillation vials containing ~5 mL EcoLume liquid scintillation cocktail for α-counting measurements. After extraction, the pcH of the aqueous phase was determined.

RESULTS AND DISCUSSION

Acid dissociation constants. The potentiometric titration curves for EDTA and TTA are shown in the Figure 1. In such titrations, for the monoprotic anions, the values of pKa were calculated by the classic *Calvin-Bjerrum* method [6], based on the average number of protons, $\boldsymbol{n}$, associated with the anionic ligand. The pK_a values for these ligands were calculated using the following equations:

$$pK_a = pcH + \log(\boldsymbol{n}-1) \tag{3}$$

where $\boldsymbol{n}$ is calculated after each addition of base by

$$\boldsymbol{n} = c_H - [H^+]/[c_L] \tag{4}$$

In this equation, c_H = total molar proton concentration and [H+] = hydrogen ion molar concentration after the addition. The values of pK_a obtained for each of the tirtration points were averaged to get the final value of pK_a. For the polyprotic ligands, the pK_a values were calculated with the use of the computer program BEST [7].

Figure 2 illustrates a typical set of spectrophotometric curves of oxine as a function of pcH. Oxine shows two strong absorption peaks at 236 nm and 252 nm that correspond to the absorptions of the associated and dissociated forms, respectively. The single isosbestic point indicates the presence of two species under the experimental conditions. The linear relationship between the absorptivities for 252 nm and the concentration of oxine at constant pcH, was used to calculate the molar absorptivity, $\varepsilon = 42152 \pm 250$ l $mol^{-1}cm^{-1}$. In analogous measurements at 267 nm wavelength, the molar absoptivity for 1,10-phenanthroline was determined, $\varepsilon = 27634 \pm 204$ l $mol^{-1}cm^{-1}$. The pKa values were obtained from the absorbance at different pcH's using the program SQUAD [8]. The pK_a values for all studied organics are presented in Table 1, which includes literature values [9] for comparison.

Complex formation constants. In this work three different techniques were used for determination of the stability constants. In solvent extraction experiments in the presence of complexing ligand, the distribution constant, D, is expressed as

$$D = [AnO_2S_2]_{(o)}/([AnO_2]_{(aq)} + [AnO_2L]_{(aq)} + ...) \qquad (5)$$

where S is the HDEHP extractant and L is the organic anion. In the absence of an organic ligand, D is represented by D_o. From the dependence of the distribution ratios for NpO_2^+ and UO_2^{+2} on the ligand concentration at constant pcH, the β_n values were calculated by the *Leden* method [6]. The slopes of a plot of $[D_0/D-1]$ vs. free ligand concentration, $[L]_f$ for the values of $[L]_f$ that resulted in a linear plot, were evaluated by linear regression to obtain β_1 . For β_2 , the distribution ratios for higher values of $[L]_f$ were used in a plot of $[D_0/D-1]/[L]_f$ vs. $[L]_f$ and the linear portion of the slope analyzed by regression analysis.

Typical curves showing the variation of $[D_0/D-1]$ with free organic ligand concentration are shown for NpO_2^+ - α-hydroxyisobutyrate system and for UO_2^{+2} - acetate system in Figure 3. The linearity of the NpO_2^+ data indicates the presence of only 1:1 complexation, whereas the nonlinear curve for UO_2^{+2} indicates higher complexation.

For NpO_2^+ complexation by ascorbate, the extraction method could not be used due to redox. The absorbance of the near-IR band of NpO_2^+ at 980 nm was measured at constant NpO_2^+ concentration, constant pcH, and various concentrations of ascorbate. A set of spectral data is presented in Figure 4. One isosbestic point was observed indicating the formation of only the 1:1 complex.

For the organics whose solubility in the organic phase is not negligible (e.g., TTA, oxine, and 1,10-phenanthroline), the extraction method could not be used. The stability constants of NpO_2^+ with TTA and oxine were determined by spectroscopy using the 980 nm band. From the spectroscopic data, the stability constants were calculated with the computer program SQUAD. NpO_2^+ formed precipitates with 1,10-phenanthroline so that the stability constant could not be determined.

The stability costants of UO_2^{2+} with TTA, oxine and 1,10-phenanthroline were determined by potentiometric titration [10]. The stability constants for NpO_2^+ and UO_2^{2+} with all the studied ligands are listed in Table 2 with literature values from [9, 11-14].

Competition with hydrolysis. In saturated NaCl solution of near neutral pH, which can represent some of the brines in a salt bed repository, hydrolysis of actinides may be the main reaction in the absence of complexation. For the hydrolysis reaction

$$M^{n+} + iH_2O \rightarrow M(OH)_i^{n-i} + iH^+ \tag{6}$$

the hydrolysis constant can be expressed by

$$^*\beta_i = \frac{[M(OH)_i^{n-i}]\,[H^+]^i}{[M^{n+}]} \tag{7}$$

The ratio of the concentration of the $[M(OH)_i^{n-i}]$ species to the free metal concentration $[M^{n+}]$, denoted by R_i, can be calculated from the hydrolysis constant as a function of pcH :

$$R_i = \Sigma\, [M(OH)_i^{n-i}]/[M^{n+}] = \Sigma^*\beta_i \;/\; [H^+]^i \tag{8}$$

The following $\log^*\beta_i$ values for NpO_2^+ and UO_2^{2+} from the literature [15] were used in these estimates: $\log^*\beta_1$ for NpO_2^+, -10; for UO_2^{2+}, -6.0; $\log^*\beta_2$ for UO_2^{2+}, -12.4. The calculated R_i value for NpO_2^+ at pcH = 6.0 is 0.0001; and pcH=7.0, 0.001; for UO_2^{2+} at pcH=6.0 it is 1.4 and at pcH=7.0, 49.8, reflecting the stronger tendency of UO_2^{2+} to hydrolyze. For the low concentrations of organic ligands, we assume formation of only the 1:1 complex. From the values of β_1, the ratio of [ML]:[M] can be calculated for a given free ligand concentration

$$[ML^{n-1}]/[M^{n+}] = \beta_1\,[L^-]_f \tag{9}$$

For the organics listed in Table 1 with pKa values of 5.0 or higher, the ligand is not fully dissociated at pcH < 7 and correction for the degree of protonation must be made using the relation

$$[L]_f = [L]_T/(10^{pKa\text{-}pcH} + 1) \tag{10}$$

where $[L]_f$ and $[L]_T$ denote free and total ligand concentration.

Using the hydrolysis constants with the complexation constants of Table 2, the total ligand concentration that produces a certain concentration of the complexed species relative to a concentration of the hydrolyzed species can be calculated from combined equations 8, 9, and 10. Table 3 presents the estimated total ligand concentrations that give a 10% effect relative to hydrolysis for pcH 6 and 7. The more extensive hydrolysis of UO_2^{2+} requires much higher concentrtions of the ligands. From Table 3, acetic, ascorbic, lactic, and α-hydroxyisobutyric acids and oxine are unlikely to be in sufficient concentration to increase UO_2^{2+} concentration significantly. By contrast, these calculations indicate that all these organics could increase the NpO_2^+ solubility as extremely low organic concentrations are required.

Acknowledgments

This work was performed as part of Waste Isolation Pilot Plant (WIPP) Actinide Source Term Program, supported at Sandia National Laboratories by the U.S. Department of Energy under Contract DE-AC04-94AL85000, and at Florida State University under contract AH 5590. We gratefully thank Dr. Craig F. Novak for many helpful comments during this study.

REFERENCES

1. McDowell, W. J., Perdue, P. T., Case, G. N., J. Inorg. Nucl. Chem. **38**, 2127 (1976) .

2. Caceci, M. S., Choppin, G. R., Radiochim. Acta **33**, 113 (1983) .

3. Taft, R. W. Jr, Cook, E. H., J. Am. Chem. Soc., **81**, 46 (1959).

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

5. Borkowski, M., Siekierski, S., Radiochim. Acta **56**, 31 (1992).

6. Hartley , F. R., Burgess, C., Alcock, R. M., "Solution Equilibria", Elis Horwood, NY., 1980.

7. Martell, A. E., Motekaitis, R. J., "Determination and Use of Stability Constants", VCH Publishers, Inc., NY 1988.

8. Leggett, D. J., "Computational Method for the Determination of Formation Constants" Modern Inorganic Chemistry, Series Editor: Fackler J. P., Jr., Plenum Press, NY 1985.

9. Martel, A. E., Smith, R. M., Motekaitis, R. J., "NIST Critical Stability Constants of Metal ", Complex Database, College Station, TX 1993.

10. Unak, P., Ozdemir, D., Unak, T., J. Radioanal. Nucl. Chem., Letters **186**, 325 (1994).

11. Rizkalla, F. N., Nectoux, F., Dabos-Seignon , S., Pages M., Radiochim. Acta **51**, 113 (1990).

12. Inoue, Y., Tochiyama , O., Polyhedron **2**, 627 (1983).

13. Stout, B. E., Caceci, M. S., Nectoux, F., Pages, M., Radichim. Acta **46**, 181 (1989).

14. Gross, J., Keller, C., J. Inorg. Nucl. Chem. **34**, 725 (1972).

15. Choppin, G. R., Mathur, J. N. Radiochim. Acta **52/53**, 25 (1991).

REFERENCES

1. McDowell W. J., Perdue P. T., Case G. N., 1976. "Purification of di(2-ethylhexyl)phosphoric acid." J. Inorg. Nucl. Chem. vol. **38**, 2127-2129 .
2. Caceci M. S., Choppin G. R., 1983. " An Improved Technique to Minimize Cation Adsorption in Neutral Solutions.", Radiochim. Acta vol **33**, 113-114.
3. Taft R. W. Jr, Cook E. H., 1959. "Rate of Equilibrium in First Complex Formation between Thenoyltrifluoroacetone (TTA) and Aqueous Metal Ions." J. Am. Chem. Soc., vol. **81**, 46-54.
4. Caceci M. S., Choppin G. R., 1983. "The Determination of the First Hydrolysis Constant of Eu(III) and Am(III)". Radiochim. Acta vol **33**, 101-104.
5. Borkowski M., Siekierski S., 1992. "Factors Affecting the Position of Y and Actinides(III) with Respect to Lanthanides in the NH4SCN-Adogen-464SCN Extraction System." Radiochim. Acta vol. **56**, 31-35.
6. Hartley F. R., Burgess C., Alcock R. M., 1980. "Solution Equilibria", Elis Horwood, NY.,
7. Martell A. E., Motekaitis R. J., 1988. "Determination and Use of Stability Constants", VCH Publishers, Inc., NY
8. Leggett D. J., 1985. "Computational Method for the Determination of Formation Constants" Modern Inorganic Chemistry, Series Editor: Fackler, J. P., Jr., Plenum Press, NY
9. Martel A. E., Smith R. M., Motekaitis R. J.,1993. "NIST Critical Stability Constants of Metal", Complex Database, College Station, TX

10. Unak P., Ozdemir D., Unak T., 1994. " Stability Constants of Uranium(VI) and Thorium(IV) Complexes Formed with 8-hydroxyquinoline and its 5-sulfonic Derivative." J. Radioanal. Nucl. Chem., Letters vol. **186**, 325-332.

11. Rizkalla F. N., Nectoux F., Dabos-Seignon S., Pages M., 1983. "Complexation of Neptunium(V) by Halo- and Hydroxycarboxylate Ligand." Radiochim. Acta vol. **51**, 113-117.

12. Inoue Y., Tochiyama O., 1983. "Study of the Complexation of Np(V) with Organic Ligands by Solvent Extraction with TTA and 1,10-phenanthroline." Polyhedron vol. **2**, 627-630.

13. Stout B. E., Caceci M. S., Nectoux F., Pages, M., 1989. "Complexes of NpO_2^+ with Aliphatic Dicarboxylic Acids." Radiochim. Acta vol. **46**, 181-184.

14. Gross J., Keller C., 1972. "Die Chalatbildung Des Funfwertigen Neptunium mit 1,3-Diketonen." J. Inorg. Nucl. Chem. vol . **34**, 725-738.

15. Choppin G. R., Mathur J. N. 1991. "Hydrolysis of Actinyl(VI) Cations." Radiochim. Acta **52/53**, 25-28.

Figure Captions :

Fig 1. Potentiometric titration curves for EDTA and TTA.
a) [EDTA]=0.001 M, titrant [NaOH]=0.01 M;
b) [TTA]=0.001 M, titrant [HCl]=0.03 M.

Fig.2 A set of spectrophotometric curves of oxine in 5.0 m (NaCl) solution as a function of pcH. [oxine]=4E-5 M.

Fig 3. The dependence of $[D_0/D-1]$ on free ligand concentration.
a) UO_2^{2+} - acetate system, b) NpO_2^+ - α-hydroxyisobutyrate system.

Fig. 4. A set of NpO_2^+ - ascorbate spectra in 5.0 m (NaCl) solution.
$[NpO_2^+]$=0.45 mM , [ascorbate]=5.0 mM - 0.4 M, pcH=5.2±0.1.

Table 1. Acid constants, pK_a, of organic ligands determined by potentiometry or spectrophotometry. I=5.0 m (NaCl), t=25°C.

Organic ligand	pK_a	pK_a (lit.) [9]
acetate	$pK_{a1} = 5.13 \pm 0.01$	4.56 (I=0.1) 4.58 (I=1.0)
lactate	$pK_{a1} = 4.23 \pm 0.05$	3.66 (I=0.1) 3.81 (I=2.0)
oxalate	$pK_{a1} = 1.28 \pm 0.01$ $pK_{a2} = 3.95 \pm 0.02$	1.0 (I=0.1) 4.27 (I=0.0)
citrate	$pK_{a1} = 3.13 \pm 0.02$ $pK_{a2} = 4.49 \pm 0.03$ $pK_{a3} = 5.35 \pm 0.01$	2.90 (I=0.1) 4.76 (I= 0.0) 6.39 (I=0.0)
ascorbate	$pK_{a1} = 4.64 \pm 0.02$	4.03 (I=0.1)
α-hydroxy isobutyrate	$pK_{a1} = 4.47 \pm 0.02$	3.79 (I=0.1)
EDTA	$pK_{a1} = 1.97 \pm 0.01$ $pK_{a2} = 2.46 \pm 0.01$ $pK_{a3} = 6.95 \pm 0.01$ $pK_{a4} = 9.01 \pm 0.03$	2.00 (I=1.0) 2.69 (I=1.0) 6.21 (I=1.0) 8.77 (I=1.0)
oxine	$pK_{a1} = 10.05 \pm 0.03$ $pK_{a12} = 5.82 \pm 0.02$	9.60 (I=1.0) 5.19 (I=1.0)
TTA	$pK_{a1} = 6.48 \pm 0.03$	6.29 (I=1.0)
1,10-phenanthroline	$pK_{a1} = 5.82 \pm 0.05$	5.17 (I=1.0)

Table 2. Stability constants of NpO_2^+ and UO_2^{2+} complexes with organic ligands.
I = 5.0 m (NaCl), pH = 5.8±0.1, t = 25° C.

Organic ligand	NpO_2^+ log β_1	log β_1(lit.)	log β_1	UO_2^{2+} log β_2	log β_1(lit.)
acetate	1.70±0.04	2.31 (I=1.0) [9] 0.87 (I=2.0) [11]	1.68±0.02	3.18±0.03	2.61 (I=0.1) [9] 2.44 (I=1.0) [9]
lactate	0.76±0.03	1.75 (I=0.1) [9] 1.11 (I=2.0) [12]	2.03±0.02	3.40±0.05	2.72 (I=1.0) [9]
oxalate	3.04±0.08	3.74 (I=1.0) [9] 3.53 (I=1.0) [13] 3.55 (I<0.1) [12]	5.50±0.02	10.60±0.02	6.36 (I=0.1) [9] 6.3 (I=4.0) [9]
citrate	2.40±0.06	2.49 (I=2.0) [11]	6.04±0.01	10.98±0.03	6.9 (I=1.0) [9]
α-hydroxy isobutyrate	0.90±0.03	1.80 (I=2.0) [11] 1.35 (I=0.01) [13]	2.11±0.02	4.02±0.03	---
EDTA	3.56±0.04	5.3 (I= 0.1) [9]	3.68±0.03	---	7.40 (I=0.1) [9]
ascorbate	0.46±0.08	0.77 (I=2.0) [11]	1.58±0.02	---	3.04 (I=0.0) [9] 2.35 (I=0.1) [9]
oxine	5.43±0.08	---	7.70±0.11	---	---
TTA	2.58±0.11	2.89 (I=0.1) [14]	6.80±0.09	---	---
1,10-phenanthroline	pptn	---	4.76±0.08	---	---

Table 3. The estimated ligand concentrations which the effect of complexation of neptynyl and uranyl ions in I = 5.0 m (NaCl) ionic strength solution is equal to 10 %of the degree of hydrolysis.

	NpO_2^+		UO_2^{2+}	
Ligand	pcH = 6.0 $[L]_T$, M	pcH=7.0 $[L]_T$, M	pcH=6.0 $[L]_T$, M	pcH=7.0 $[L]_T$, M
acetate	2.2E-07	2.0E-06	3.1E-03	1.0E-01
ascorbate	3.6E-06	3.5E-05	3.8E-03	1.3E-01
lactate	1.8E-06	1.7E-05	1.3E-03	4.7E-02
α-hydroxy isobutyrate	1.3E-06	1.3E-05	4.9E-04	1.7E-02
citrate	4.0E-08	4.0E-07	1.3E-07	4.5E-06
EDTA	3.2E-09	3.2E-08	1.7E-06	6.0E-05
oxalate	9.1E-09	9.1E-08	4.4E-07	1.6E-05
oxine	4.2E-07	4.2E-06	3.1E-05	1.1E-04
TTA	1.0E-07	3.4E-07	8.8E-08	1.0E-06
phenanthroline	---	---	4.2E-06	9.3E-05

Determination of dissociation constant
Potentiometric titration in 5.0 m NaCl

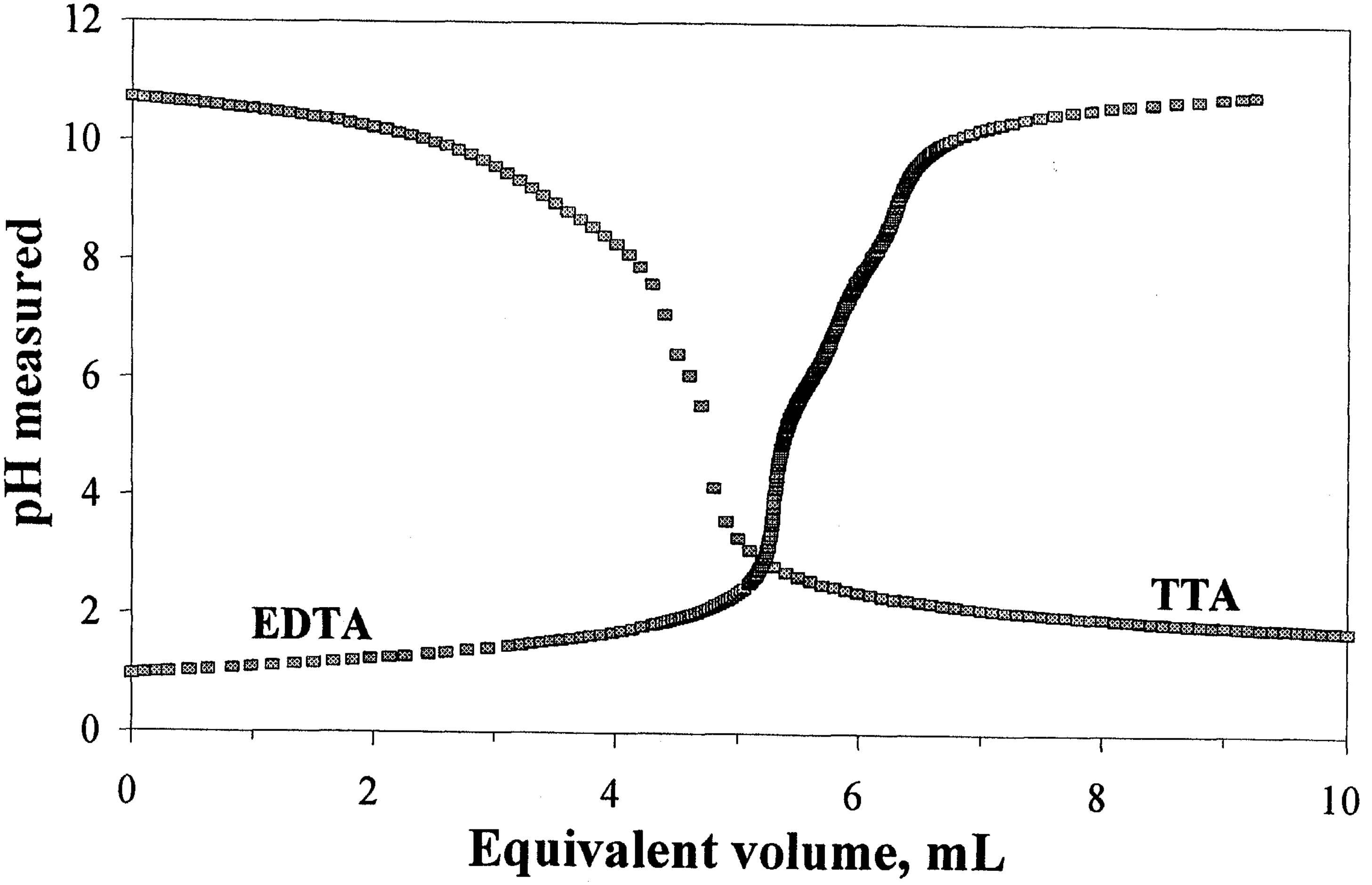

Fig 1.

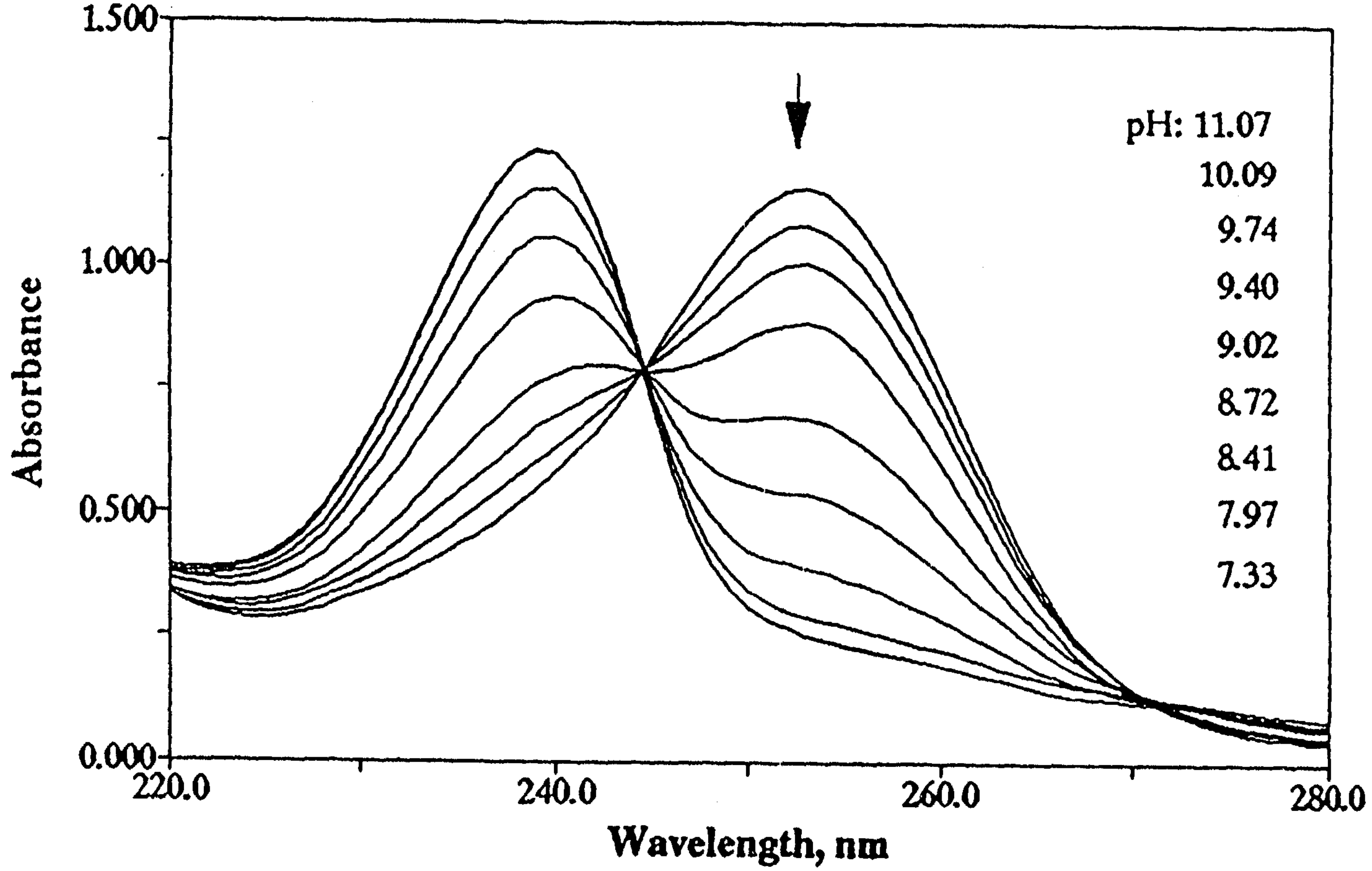
1.500
1.000
0.500
0.000
Absorbance
220.0
240.0
260.0
280.0
Wavelength, nm
pH: 11.07
10.09
9.74
9.40
9.02
8.72
8.41
7.97
7.33

Fig. 2

Determination of stability constants
Extraction with HDEHP, I=5.0 m (NaCl)

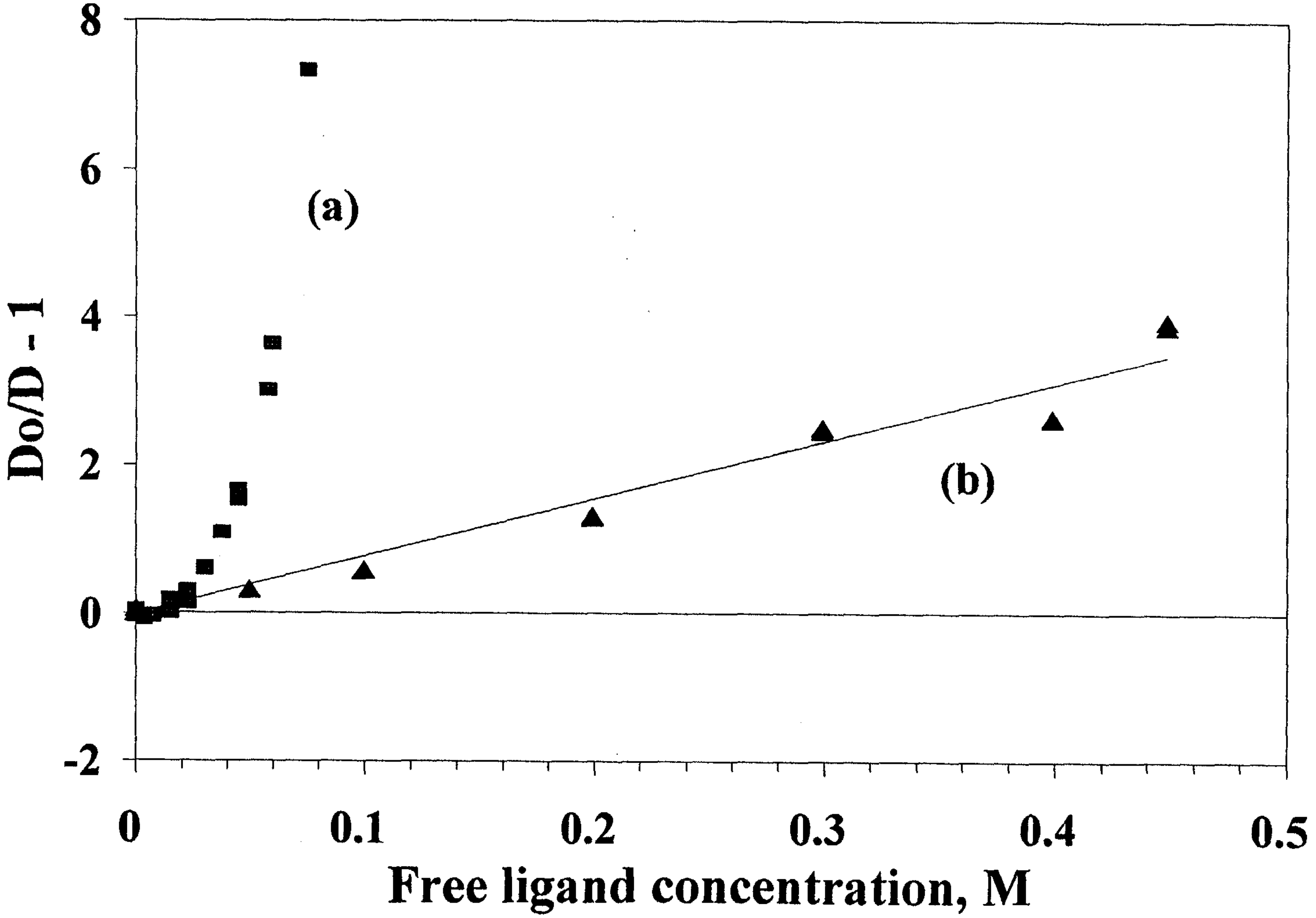

Fig 3

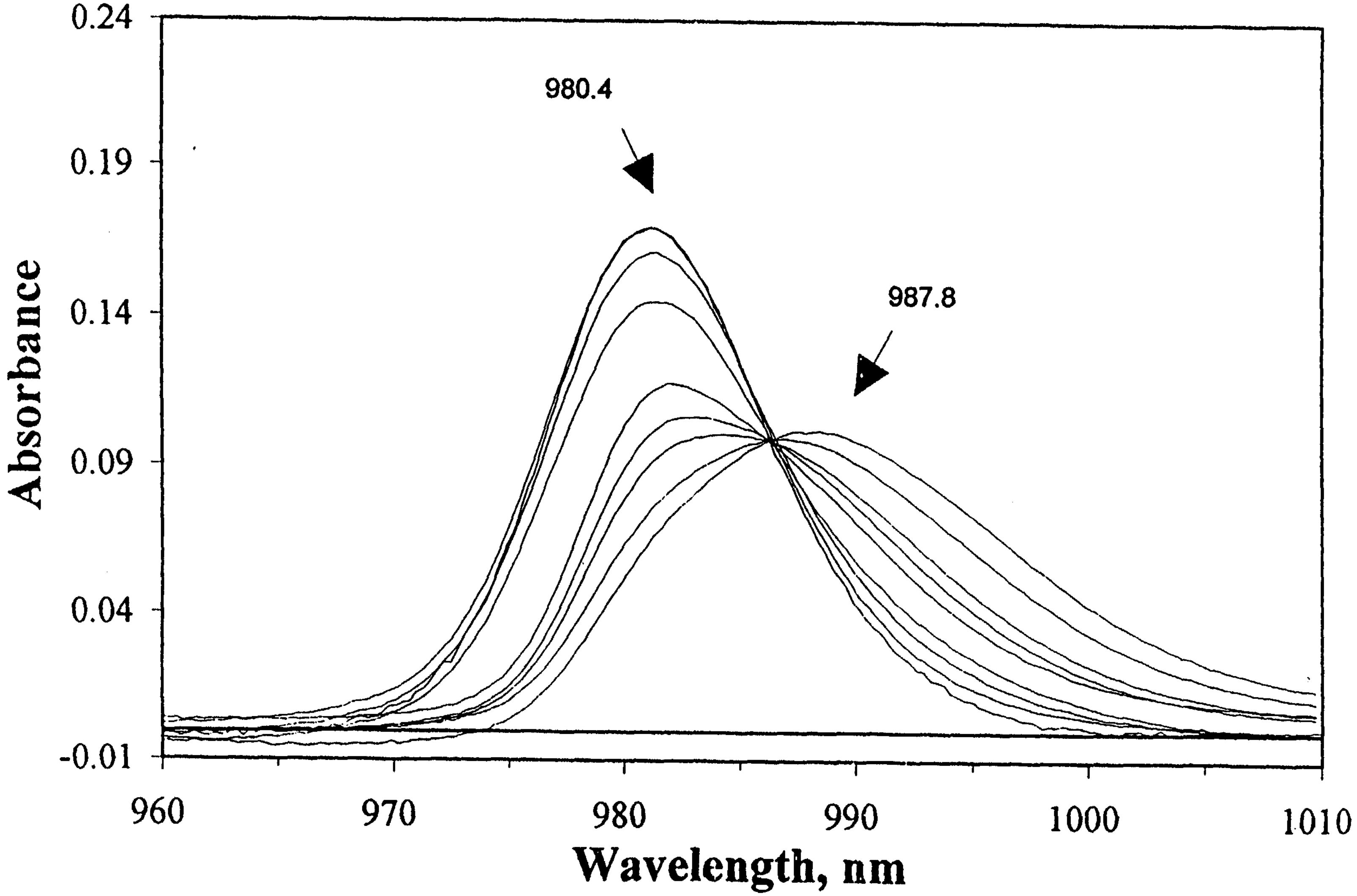
980.4
987.8
0.24
0.19
0.14
0.09
0.04
-0.01
Absorbance
960
970
980
990
1000
1010
Wavelength, nm

Fig 4