

**Hydrophilic actinide complexation
studied by solvent extraction
radiotracer technique**

Jan Rydberg

Department of Nuclear Chemistry, Chalmers University
of Technology, Gothenburg, Sweden and Radio-
chemistry Consultant Group AB, V. Frölunda, Sweden

October 1996

HYDROPHILIC ACTINIDE COMPLEXATION STUDIED BY SOLVENT EXTRACTION RADIOTRACER TECHNIQUE

Jan Rydberg

Department of Nuclear Chemistry, Chalmers University of
Technology, Gothenburg, Sweden and
Radiochemistry Consultant Group AB, V. Frölunda, Sweden

October 1996

This report concerns a study which was conducted for SKB. The conclusions and viewpoints presented in the report are those of the author(s) and do not necessarily coincide with those of the client.

Information on SKB technical reports from 1977-1978 (TR 121), 1979 (TR 79-28), 1980 (TR 80-26), 1981 (TR 81-17), 1982 (TR 82-28), 1983 (TR 83-77), 1984 (TR 85-01), 1985 (TR 85-20), 1986 (TR 86-31), 1987 (TR 87-33), 1988 (TR 88-32), 1989 (TR 89-40), 1990 (TR 90-46), 1991 (TR 91-64), 1992 (TR 92-46), 1993 (TR 93-34), 1994 (TR 94-33) and 1995 (TR 95-37) is available through SKB.

**HYDROPHILIC ACTINIDE COMPLEXATION
STUDIED BY
SOLVENT EXTRACTION RADIOTRACER
TECHNIQUE**

Jan Rydberg

Department of Nuclear Chemistry
Chalmers University of Technology,
S-412 96 Gothenburg, Sweden,

and

Radiochemistry Consultant Group AB
Tigerstigen 11
S-42672 V. Frölunda, Sweden

October 1996

ABSTRACT

Actinide migration in the ground is enhanced by the formation of water soluble complexes between the actinide ions (*central atoms*) and inorganic and/or organic complex formers (*ligands*) dissolved in the ground water. It is essential to the risk analysis of a wet repository to know the concentration of the central atoms and the ligands in the ground water, and the stability of the complexes formed between them (the *complex formation constant*); from such data the concentration of all dissolved actinide species can be calculated, and -- using additional data on sorption, diffusion, and ground water flow rate-- the migration rate of the actinides in the ground can be predicted.

The important actinides in nuclear waste are U, Np, Pu and Am, all radioactive and with half-lives long enough to allow the determination of their macroscopic properties, usually at $>10^{-4}$ M. However, when dissolved in nature, their concentrations are hardly macroscopic; typical concentration values are $<10^{-7}$ M (*trace concentrations*). Because the chemical behavior at trace concentrations often differ from that at macro concentrations (for example polynuclear complex formation), it is important to know the chemical behavior of actinides at trace concentrations in the ground water. One method commonly used for such investigations is the *solvent extraction radiotracer (SXRT)* technique, by which the radioactive properties of the actinides are used for their detection.

This report describes the SXRT technique in some detail. A particular reason for this analysis is the claim that complex formation constants obtained by the SXRT technique differs even at same actinide concentration, or are less reliable than results obtained by alternative techniques. It is true that several difficulties are encountered in the application of the SXRT technique to actinide solutions, as for example redox instability, hydrophilic complexation by side reactions and sorption, but it is also shown that a careful application of the SXRT technique yields results as reliable as by any other technique.

The report contains a literature survey on solvent extraction studies of actinide complexes formed in aqueous solutions, particularly by using the organic reagent thenoyltrifluoroacetone (TTA) dissolved in benzene or chloroform (Table 1). Hydrolysis constants obtained by solvent extraction are listed in Table 9. The last two tables contain all actinide complexes studied by SX with inorganic ligands (Table 11) and with organic ligands (Table 12).

Part of this work was done under the auspices of the OECD/NEA Nuclear Data Group through the support of the Swedish Nuclear Fuel and Waste Management Co (SKB).

SAMMANFATTNING

Aktinidernas rörlighet i grundvatten ökas om vattenlösliga komplex bildas mellan aktinidjonerna (*centralatomer*) och oorganiska eller organiska komplexbildare (*ligander*) i grundvattnet. Vid riskanalys av ett avfallslager beläget i våt berggrund är det viktigt att veta såväl halter av aktinider och ligander i vattnet som jämviktskonstanter för bildning av vattenlösliga aktinidkomplex; från sådana data-- tillsammans med data om sorption, diffusion och grundvattnets rörelser -- kan aktinidernas halt och vandringshastighet i marken förutsägas.

De viktigaste aktiniderna i avfallet är U, Np, Pu och Am, vilka alla är radioaktiva men med så långa halveringstider att deras egenskaper kan mätas med makroskopiska metoder, dvs i halter $>10^{-4}$ M; sådana metoder har därför också i stor utsträckning använts för studier av bildning av aktinidkomplex. I grundvatten från ett läckande avfallslager kommer emellertid aktinidernas halter bli mycket lägre, ofta $<10^{-7}$ M (*spårhalter*). Då aktinidjoner många gånger uppför sig olika vid makromängder och i spår mängder (t.ex. polymerbildning vid hydrolys), är det för säkerhetsanalysen nödvändigt att också ta hänsyn till egenskaperna i spår mängder. Ett sätt att studera detta är medelst vätskeextraktion med radiometrisk detektering (*solvent extraction radiotracer*, SXRT, teknik).

Denna rapport beskriver relativt ingående SXRT tekniken och dess felkällor, bl.a. när det hävdats att denna teknik även vid samma aktinidhalter ger jämviktskonstanter som systematiskt avviker från vad som erhålles med alternativa tekniker. SXRT tekniken tillämpad på aktiniderna kräver speciell uppmärksamhet i avseende på ett flertal faktorer (t.ex. redoxjämvikter, sorption och hydrofil komplexbildning), men det kan visas att vid noggran tillämpning av denna teknik erhålles jämviktskonstanter i överensstämmelse med vad som fås med annan teknik (vilken också förutsättes tillämpas med stor omsorg).

Rapporten innehåller en litteraturöversikt över hydrofil komplexbildning av aktinider studerad med SXRT teknik, särskilt med användning av thenoyltrifluoroacetone (TTA) löst i benzene eller kloroform (Tabell 1). Med SXRT bestämda aktinidhydrolyskonstanter har samlats i Tabell 9, komplex med andra oorganiska ligander i Tabell 11, och med organiska ligander i Tabell 12.

Detta arbete har utförts i samråd med OECD/NEA Nuclear Data Group och med stöd av Svensk kärnbränslehantering (SKB) AB.

TABLE OF CONTENTS

	Page
1. Actinide wastes	1
2. Actinide complexation	1
3. The solvent extraction radiotracer technique (SXRT)	2
3.1 Solvent extraction	2
3.2 Radiometric methods	3
3.3 The SXRT technique	3
4. Extraction equilibria	4
4.1 The chemical system	4
4.2 The extraction constant	5
4.3 Aqueous complexation	7
4.3.1 Hydrolysis	7
4.3.2 Other hydrophilic complexants (than OH ⁻)	9
4.3.3 Hydrophilic complexes of the extractant; determination of [A ⁻]	9
4.3.3 Several hydrophilic M-complexes	12
4.4 Adduct formation	13
4.5 Complexes between the metal and the ionic medium	14
4.6 Other considerations	14
4.6.1 Activity factors	14
4.6.2 Kinetics	15
5. Experimental aspects on the SXRT technique	15
5.1 The distribution ratio	15
5.2 Radiometric technique	16
6. Actinide redox equilibria	17
6.1 Effect of impure valency state	17
6.2 The air-water system	18
6.3 Presence of strong reductant	19
6.4 Effect of hydrolysis of An(III) and An(IV)	19
6.5 Effect of other hydrophilic complexes	20
7. Actinide hydrolysis	21
7.1 Hexavalent state	21
7.2 Pentavalent state	21
7.3 Tetravalent state	23
7.4 Trivalent state	23
8. Formation of other hydrophilic complexes	24
8.1 Inorganic ligands	24
8.2 Organic ligands	24
9. Comparison between the SXRT and other techniques	24
10. Conclusions	29
11. References	30

This survey covers the aqueous complexation of actinides as investigated by *solvent extraction* using *radioactive tracers* for the actinide ions. The review presents the equilibrium equations and points out the difficulties (and advantages) appearing in the technique. The review is comprehensive with respect to actinide hydrolysis studies, but more less so in respect to other ligands.

Recognition is given to the OECD Nuclear Energy Agency Data Bank for permission to use part of the material gathered for their publications (97NEA-TDB) and to the Swedish Nuclear Fuel and Waste Management Co for financial support.

1. ACTINIDE WASTES

In 1995 nuclear energy contributed 17% to the world's electricity production. Most of this energy came from fissioning of uranium (about 62%) and of plutonium (about 38%) isotopes, the latter having been formed through capture of neutrons in uranium isotopes followed by radioactive decay. In the n-capture/decay process also neptunium and heavier actinides (Am, Cm, Bk, Cf) are formed. The annual amounts of actinides left in spent uranium fuel from the global nuclear energy program of $\approx 340 \text{ GW}_{\text{el}}$ (1995) are listed in the Table below (spent fuel age: 10 years after removal from the reactors):

U	Np	Pu	Am	Cm
9500 tons	4.4 tons	≈ 90 tons	2.8 tons	170 kg

The amount of Cf is about 1 mg and of Bk about 1 μg . As it is likely that the contribution of nuclear energy will continue to rise, so will also the global amounts of transuranium actinides. The small amount of the nuclear energy produced from thorium fueled reactors will also produce an actinide waste (mainly Th+Pa+U). Of course, in addition to actinides, the waste will contain large amounts of fission products.

As the actinides are biologically harmful when taken into the body (e.g. the annual limit of intake of ^{239}Pu is 17 μg), they must be stored away from biological life. Many options are available and have to some extent also been explored, but the deposition in geologic repositories seem to be the present choice among both the nuclear energy producers and the regulatory authorities. There seem also to be a consensus on the belief that in the long time scale, deposited nuclear waste may ultimately be released into water streams. Thus it is considered necessary to know how the actinides in the waste behave when exposed to groundwater, so that the risk to man can be properly evaluated. The actinides dissolve very slowly -- and slightly -- in groundwater, primarily through complexation by groundwater anions; this increases the mobility of the actinides in the biosphere.

It should be noted that in the nuclear fuel cycle which comprises reprocessing and recycling of the transuranics, the nuclear wastes contain insignificant amounts of actinide elements.

2. ACTINIDE COMPLEXATION

Considerable knowledge has been acquired on the aqueous complexation of the actinides, particularly through work on uranium using electrochemical and spectrometric techniques. Quite a number of ionic actinide species are produced in water. As groundwater usually contains a large number of anions (carbonate, chloride, fluoride, etc)

they complex the actinide ions to different degrees depending on the actinide valency state (+3, +4, +5 or +6), pH, etc. For actinides other than uranium, and particularly those which are not available in substantial amounts, solvent extraction has been a favored technique, using trace concentrations (usually $<10^{-6}$ M) of the radioactive metals; we refer to this as the Solvent Extraction RadioTracer (SXRT) technique. When comparing equilibrium constants determined by this technique with other "more established" ones, it has often been observed that the solvent extraction radiotracer technique yields larger formation constants. This is demonstrated in Figure 1 for the hydrolysis of tetravalent actinides. Because the SXRT technique also is commonly applied to non-actinide metal systems, the discrepancy becomes a fundamental chemical problem: One may ask if there is an inherent "fault" in the SXRT technique, or, perhaps that all the other techniques have (other) inherent faults (cf. 83CAC/CHO.2)?

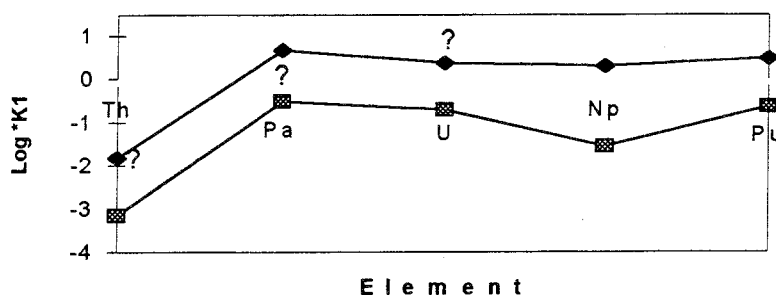


Figure 1. Variation in the first hydrolysis constant $*K_1$ with atomic number Z for tetravalent actinides; upper line refers to SX-tracer experiments, lower line to experiments on macroscopic concentrations (77DUP/GUI).

Occasionally, any method for determination of physical constants must be questioned with respect to reliability of experimental technique, mistakes in theory and computational errors. This paper therefore begins with a critical review of the SXRT technique, *per se*. When the SX experiments are controlled, the theory is simple to develop and use to derive equilibrium constants by graphical or other computational techniques. In the second part, the complexation studies are presented. The results are compared with other techniques at the end of this paper.

3. THE SOLVENT EXTRACTION RADIOTRACER TECHNIQUE, SXRT

3.1 Solvent extraction

Solvent extraction (or, liquid-liquid distribution) has been shown to be an efficient large-scale chemical separation technique (92RYD/MUS/CHO, 96SHA/PAI/PRV). Less known is its application to studies of complex formation. The basic principle was laid down almost exactly 100 years ago by Nernst and co-workers: The distribution of a species of given chemical composition between two immiscible solvents is constant and independent of the concentration and of other species (the *Nernst distribution law*). We abbreviate the *distribution constant* K_D :

$$K_D = \{\text{Species I}\}_{\text{organic phase}} / \{\text{Species I}\}_{\text{aqueous phase}} = \gamma_{\text{org}} [\text{Spec. I}]_{\text{org}} / \gamma_{\text{aq}} [\text{Spec. I}]_{\text{aq}} \quad (\text{Eq. 1})$$

Here $\{\}$ refer to chemical activities, γ to activity factors, $[]$ to concentrations, and index aq and org to the two liquid phases; fat italics is used for thermodynamic constants. Expression (1) defines the terminology used here.

Already in 1902 Morse (02MOR) applied this principle to the study of mercury complexation by halides in water, measuring the distribution of mercury between toluene and water, using the observation that the uncharged mercury halide complex HgX_2 was soluble in the organic phase, but no other mercury species. In 1938 Grahame and Seaborg (38GRA/SEA) demonstrated the validity of the Nernst distribution law at radioactive trace concentrations.

Inorganic metal complexes are usually not soluble in organic solvents, and therefore solvent extraction would not appear to be an applicable technique for studying aqueous metal complexation. However, in 1941 Kolthoff and Sandell (41KOL/SAN) showed that many metals could easily be complexed with organic chelate formers (below referred to as *extractants*), yielding neutral metal-organic complexes, which are soluble in organic solvents; they showed that—for analytical purposes—metals could easily be separated from each other by solvent extraction at different pH's.

With the synthesis of a number of fluoride substituted beta-diketones, among them *thenoyltrifluoroacetone*, commonly named TTA, Reid and Calvin (50REI/CAL) made a new group of powerful extractants available. Using TTA dissolved in benzene, Connick and McVey (49CON/MCV) in the late 1940:ies demonstrated that solvent extraction could be an efficient tool for studying complexation in aqueous solutions, in this case hydroxide, sulfate and fluoride complexes of zirconium in aqueous NaClO_4 , using the radioactive tracer ^{95}Zr . From then on a number of important pioneering papers appeared (49IRV/WIL, 50RYD, 52MAR/CAL, etc), establishing solvent extraction as a convenient method for studying aqueous complexation of metals at tracer concentration (usually $\leq 10^{-6}$ M). In the following we shorten the name for this technique to SXRT for Solvent Extraction RadioTracer; it may be noted that solvent extraction can also be used for complex formation studies with sensitive non-radioactive detection methods.

3.2. Radiotracer technique

Although thorium and uranium are rather common elements in nature (about as common as lead), all other actinides are rare, and the transuranium elements can only be obtained through nuclear reactions. The elements are unstable, each consisting of only radioactive isotopes. Consequently, except for Th and U, all actinides have been studied initially by radioactive methods on trace amounts of the isotopes. Although radioactive tracer methods were developed in the time period 1896-1939, it may be fair to say that it was in the Manhattan Project during World War II that this method became refined into a research routine, amply described in numerous modern textbooks (e.g. 93ADL/GUI, 95CHO/LIL/RYP). The application of this technique to solvent extraction studies of the actinides requires, however, some special considerations, as discussed in Sect. 5.

3.3 The SXRT technique

The SXRT technique requires (a) a solvent extraction system, i.e. a two-phase liquid-liquid system (usually water and an organic solvent like benzene) containing a metal ion M^{2+} and an extractant (e.g. the acid HA) forming an uncharged complex (e.g. MA_2), which is soluble in the organic phase, and (b) a radioactive isotope of the metal in high

specific radioactivity ($> 10^{10}$ bequerel/mole), which isotope must be randomly distributed between all present valency states and complexes of the metal.

The main parameter measured is the "radioactivity distribution", i.e. the ratio D_I of the radioactivity concentration (in bequerel/liter, Bq/l)¹ of the organic phase, I_{org} , to that in the aqueous phase, I_{aq} , i.e.

$$D_I = I_{org}/I_{aq} \quad (\text{Eq. 2})$$

If ϕ is the radiometric detection efficiency (which may have different values for the two different phases, see Sect. 5), then

$$[M_{tot}]_{org} = \phi_{org} I_{org} \quad \text{and} \quad [M_{tot}]_{aq} = \phi_{aq} I_{aq} \quad (\text{Eq. 3})$$

where $[M_{tot}]$ signifies the total metal concentration (sum of all species) in the indicated phase. Thus, the ratio of the total metal concentrations of the two phases is given by

$$D_M = [M_{tot}]_{org} / [M_{tot}]_{aq} = \phi_{org} I_{org} / \phi_{aq} I_{aq} = \text{const. } D_I \quad (\text{Eq. 4})$$

D_M , often simply referred to as *the distribution ratio*, is measured as a function of important variables as described below. From the analysis of such data, hydrolysis and complex formation constants can be derived. Note that eq. 1 and eq. 4 are not mutually exchangeable: while K_D is a thermodynamic constant (in bold italics), D_M is a measured quantity (only italics).

The metal distribution ratio between the organic and aqueous phases is our dependent quantity which is measured as a function of changes in the composition of the chemical system.

4. EXTRACTION EQUILIBRIA

4.1 The chemical system

The knowledge on actinide hydrolysis is good for some actinides in some valency states, for others it is poor or contradictory. Below we list the different valency states investigated in aqueous solutions. In boldface we indicate for which states the SXRT technique has been used.

hexavalent: **U, Np, Pu, Am**
 pentavalent: **Pa, U, Np, Pu**
 tetravalent: **Th, Pa, U, Np, Pu, Am**
 trivalent: **Ac, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm**

The most widely used extractant in these studies is thenoyltrifluoroacetone, more commonly known as TTA. It is a β -diketone with weak acidic properties; the reagent is therefore sometimes abbreviated HTTA. Many other β -diketones have been used: acetylacetone, benzoylacetone, etc. They can all be treated as a monobasic weak acid HA. Another equally popular extractant with similar properties is di-2-ethylhexyl phosphoric acid (D2EHP, or HDEHP), and dinonylnaphthalene sulphonic acid (DNNS). Also amines (TOA) and adduct formers like tributylphosphate (TBP) and trioctylphosphineoxide (TOPO), have been used; as they require another hydrophilic complex former (than ClO_4^-),

¹ *Specific radioactivity* is defined as radioactivity in becquerel per unit mass or volume, i.e. Bq/mole, Bq/l, etc. Radioactivity concentration is an alternative expression. (95CHO/LIL/RVD).

we shall not complicate this review by discussion also them (see e.g. 77SEK/HAS). We limit this review to the HA-type extractant, particularly TTA.

We here consider three types of ligands for actinide ions:

- (i) the extractant thenoyltrifluoroacetone (or similar extractant), abbreviated HA, which in water partly dissociates into H^+ and A^- ;
- (ii) OH-ions which cause actinide hydrolysis:
- (iii) an additional hydrophilic ligand in the aqueous phase, denoted X^- .

We consider these ligands one at a time. In practice, they may all be present at the same time, as we discuss later. Although the actinide ions can appear in different oxidation states (sometimes simultaneously), we, for the moment, represent all of them with a single species M^{z+} (valency state $+z$).

4.2 The extraction constant

In the aqueous phase the extractant HA dissociates partly into H^+ and A^- . The extractant anion A^- reacts with the metal ion M^{z+} to form the extractable uncharged complex MA_z . *The basic a priori principle* is that the only species of M in the aqueous phase is M^{z+} and in the organic phase MA_z ; thus

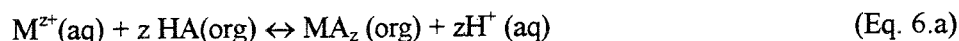
$$[M_{tot}]_{aq} = [M^{z+}]_{aq} \quad (\text{Eq. 5.a})$$

$$[M_{tot}]_{org} = [MA_z]_{org} \quad (\text{Eq. 5.b})$$

and

$$D_I = D_M = [MA_z]_{org} / [M^{z+}]_{aq} \quad (\text{Eq. 5.c})$$

The simple *extraction reaction* can be described by



and the *extraction constant* K_{ex} as

$$K_{ex} = [MA_z]_{org} [H^+]_{aq}^z / [M^{z+}]_{aq} [HA]_{org}^z \quad (\text{Eq. 6.b})$$

Then

$$D_I = D_M = K_{ex} [HA]_{org}^z [H^+]_{aq}^{-z} \quad (\text{Eq. 6.c})$$

Omitting the index "aq" for aqueous concentrations, and + and - for ionic charges, when this cannot be misunderstood, and representing chemical activities by $\{ \}$, eqn. 6.b and 6.c are replaced by

$$K_{ex} = \{MA_z\}_{org} \{H\}^z / \{M\} \{HA\}_{org}^z \quad (\text{Eq. 6.d})$$

and

$$D_I = D_M = K_{ex} \{HA\}_{org}^z \{H\}^{-z} (\gamma_M / \gamma_{MA_z,org}) \quad (\text{Eq. 6.e})$$

where γ_M is the chemical activity coefficient for M^{z+} in the aqueous phase, and $\gamma_{MA_z,org}$ for MA_z in the organic phase. Here $[M]$ is the concentration of *free* M^{z+} in the aqueous phase, and $[HA]_{org}$ is the concentration of *free* HA in the organic phase. When the chemical activity in the solution is kept constant, a plot of $\log D_M$ versus $\log [HA]_{org}$ (or $\{HA\}_{org}$) at constant $\{H^+\}$ yields a straight line of slope z , from which the K_{ex} value may be determined. The validity of Eq. 6 was first demonstrated by 49CON/MCV. If instead

Table 1. Extraction constants, K_{ex} , for actinide complexes MA_z in aqueous ClO_4^- at 25°C.Metal ion, Log K_{ex} , Ionic strength, Salt medium, $[H^+]_{aq}$, $[HTTA]_{org}$, Reference:

<i>Organic phase: chloroform</i>					
Metal ion	log K_{ex}	μ M	$[H^+]$ M	$[HA]_{org}$ M	Reference
Be(II) [#]	-1.7*	1.0 Na, H	≤ 1.0	0.1	68RUD/SEV/LAN
Y(III) [#]	-8.55	0.1		0.1	68SCH
Am(III)	-9.20	0.1		0.1	68SCH
Am(III)	-9.13	0.1	?	0.5	69KEL/SCH
Cm(III)	-9.15	0.1	?	0.5	69KEL/SCH
	-7.30	0.1	?	0.5	" (15)**
Cf(III)	-8.31	0.1	?	0.5	69KEL/SCH
	-7.48	0.1	?	0.5	" (15)*, **
Th(IV)	0.0	1.0		0.01-0.1	67SCH
<i>Organic phase: benzene</i>					
Metal ion	log K_{ex}	μ M	$[H^+]$ M	$[HA]_{org}$ M	Reference
Y(III) [#]	-6.8			0.3	63STO
La(III) [#]	-9.79	2.0		<0.5	72KAS/KER
Ho(III) [#]	-7.25	0.1		0.5	61POS/FOR
U(III)	-8.2				97NEA-TDB
Pu(III)	-2.5 ?	0.2 H, Li	$\geq 10^{-6}$	$\geq 10^{-4.5}$ norm	75HUB/HUS/GUI
Pu(III)	-8.0				97NEA-TDB
Am(III)	-7.97	0.5	pH 5.6	normalized	67ERM/STA
Am(III)	-8				69DES/HUS/GUI
Am(III)	-7.92	0.1		0.5	71ERM/VOR/ZAI
Cm(III)	-7.84	0.5	pH 5.6	normalized	67ERM/STA
Cm(III)	-7.80	0.1 h, Li	$\geq 10^{-5}$	0.004 norm.	69DES/HUS
Bk(III)	-7.60				77DUP/GUI
Cf(III)	-7.11	0.5	pH 5.6	normalized	67ERM/STA
Cf(III)	-7.10				77DUP/GUI
Fm(III)	-6.80	0.5	ph 5.6	normalized	67ERM/STA
Zr(IV)	ca. 9	2.0	2.0	0.1 M	49CON/MCV
Zr(IV)	8.0	2.0	2.0	<0.1	53LAR/TER
Hf(IV)	6.6	2.0	2.0	<0.1	53LAR/TER
Th(IV)	0.8	3.0	0.12	0.086	51ZEB/ALT/HEU
Th(IV)	0.9	3.0 Li, H			51ZEB/ALT/HEU, 52WAG/STO
U(IV)	5.5	1.0	1.0	0.05	55DAY/WIL/HAM
U(IV)	5.6				50BET/LEI
Np(IV)	5.6	2.0			54SUL/HIN, 61POS/FOR
Np(IV)	5.2	1.0 Li, H	$\geq 10^{-3}$	0.2	77DUP/GUI
Np(IV)	5.7				54SUL/HIN
Pu(IV)	6.85	1.0 H			61POS/FOR
Pu(IV)	7.33	1.0	$\geq 10^{-5}$	normalized	72MET/GUI
U(VI)	-2.0	2.0		0.5	54DAY/POW, 64FOT/FRE
U(VI)	-2.0	2.0	0.05	0.5	54DAY/POW

*) at 17-20°C

**) 56DYR, giving other references. Ref. (15) in 69KEL/SCH not given.

#) Included for comparison

{HA} is kept constant while {H⁺} is varied, a plot of log D_M against log {H⁺} (i.e. -pH) yields a straight line of slope -z. This is a more common check of the validity of Eqn. 6. Table 1 contains K_{ex} and K_{ex} values reported for the actinide-TTA system. Note that each constant refers to a specific aqueous / organic solvent system. An extensive list of K_{ex} values (as well as K_a , K_{DC} , K_{DR} and K_{add} values) for extraction of actinides by beta-diketones is given in 78STA/FRE and 86KAT/SEA/MOR.

4.3 Aqueous complexation

In this survey we only consider mononuclear complexes. This has several practical aspects: (i) The equations become much simpler to deal with, (ii) except in hydrolysis, mononuclear complexes are more common in nature, (iii) an important application of equilibrium constants is in the fields of nuclear waste and environmental systems, where in general quite dilute solutions are encountered and no polynuclear complexes are formed. Also, the SXRT technique seems only to have been applied to monomeric complexes. We avoid discussion of mixed complexes; however, these are probably more common than indicated in the past studies.

We do not describe how to use the measured values of the variables to calculate the equilibrium constants. There are quite a number of text-books describing both graphical and numerical solutions to this problem (e.g. 61ROS/ROS, 70BEC, 80HAR/BUR/ALC, 88MEL/HAV/HÖG).

4.3.1 Hydrolysis

Actinide hydrolysis has been extensively reviewed in comprehensive monographs (e.g. 75AHR/LIL/RYS, 86AHR, 92GRE/FUG/KON, 95SIL/BID/RAN, 97NEA-TDB); we therefore only briefly summarize the conditions of importance for the SXRT technique.

In dilute solutions it is assumed that the actinide forms a number of successive hydrolysis products MOH^{z-1} , $M(OH)_2^{z-2}$, $M(OH)_p^{z-p}$. In more concentrated solutions, and possibly also at high pH's in dilute solutions, polynuclear complexes $M_m(OH)_p^{mz-p}$ are formed. An advantage of the SXRT method is that in general the metal concentration is so low (preferably $\ll 10^{-6}$ M) that polynuclear complexes can be ignored (see also Sect. 5). This assumption must of course be tested, and the simplest (and common) test is to vary the total actinide concentration; if the same distribution ratio is obtained at, say 10^{-5} and 10^{-6} M $[M_{tot}]$, polynuclear complexation can be neglected, as can be seen from the equilibrium equations (see Refs.). Thus, using concentration values,

$$[M_{tot}]_{aq} = M^{z+} + MOH^{z-1} + M(OH)_2^{z-2} + M(OH)_3^{z-3} + \dots = [M^{z+}] \sum_0^p \beta_p [OH]^{-p} \quad (\text{Eq. 7})$$

where p is taken over all species (for An(IV) it is claimed that p can reach 5, but for other actinide valency states it is less) and the hydrolysis product β_p is defined by:

$$\beta_p = [M(OH)_p^{z-p}] [M^{z+}]^{-1} [OH]^{-p} \quad (\text{Eq. 8.a})$$

From the hydrolysis product of water,

$$[H^+] [OH] = K_w \quad (\text{Eq. 9})$$

introduced in eq. 7, one finds

$$[M_{tot}]_{aq} = [M^{z+}] \sum \beta_p K_w^p [H^+]^{-p} \quad (\text{Eq. 10a})$$

Eq. (8.a) is commonly written in protonated form:

$${}^* \beta_p = [M(OH)_p^{z-p}] [M^{z+}]^{-1} [H^+]^p \quad (\text{Eq. 8.b})$$

${}^* \beta_p$ is referred to as the acid (or protonated) hydrolysis constant.²

Hydrolysis depends on the pH of the solution, of course, and the hydrolysis constants β_p can -- in principle -- be determined according to eq. (8.b) from measurements of $[M^+]$ and pH by conventional techniques, e.g., potentiometry. However, in the SXRT technique, we have to consider the extraction of the MA_z complex. Thus, from

$$[M_{\text{tot}}]_{\text{org}} = [MA_z]_{\text{org}} \quad (\text{Eq. 11.a})$$

and

$$[M_{\text{tot}}]_{\text{aq}} = [M^{z+}] \sum \beta_p [OH^-]^p \quad (\text{Eq. 11.b})$$

one obtains the distribution ratio

$$D_M = [MA_z]_{\text{org}} / [M^{z+}] \sum \beta_p K_w^p [H^+]^p \quad (\text{Eq. 11.c})$$

Introducing the extraction constant (6.b)

$$D_M = K_{\text{ex}} [HA]_{\text{org}}^z [H^+]^{-z} / \sum \beta_p K_w^p [H^+]^p \quad (\text{Eq. 12})$$

In the absence of hydrolysis (i.e. $\beta_0=1$ and all other β_p 's=0), eq. (12) becomes

$$D_M^\circ = K_{\text{ex}} [HA]_{\text{org}}^z [H^+]^{-z} \quad (\text{Eq. 13.a})$$

This relation is the *normalized distribution ratio* (absence of M-complexes in the aqueous phase, according to our basic *a priori* principle); we index it by an o-mark. The ratio between eqns. (12) and (13) is

$$D_M^\circ / D_M = \sum \beta_p K_w^p [H^+]^p \quad (\text{Eq. 14})$$

From measurements of D_M as a function of $[H^+]$, the hydrolysis constants β_p can be determined. This requires that D_M° is constant; that is to say that eq. (13) must be constant, which it is as long as

- (i) the sole complex formed between M and A is MA_z , and only in the organic phase, and that no MA_n (or other M-) complexes are formed in the aqueous phase,
- (ii) z is constant (we shall loosely denote that z-value as the "ligand extraction number" N);

(iii) $[HA]_{\text{org}}$ and $[H^+]$ are known, noting that for each experiment carried out at different pH there is a normalized D_M° for each pH and $[HA]_{\text{org}}$ value. Eq. (14) shows that the extraction constant K_{ex} does not have to be known in order to determine the hydrolysis constants β_p .

For the extractant TTA, the ligand extraction numbers for the different actinide valency states are

N=3 for An(III) MA_3 (i.e. z=3); see also Sect. 4.4

N=4 for An(IV) MA_4 (z=4),

² In accurate investigations, the chemical activity must be controlled, and using chemical activities eqn. 10.a takes the form

$$\{M_{\text{tot}}\}_{\text{aq}} = [M^{z+}] \gamma_M \sum \beta_p K_w^p \{H^+\}^p \quad (\text{Eq. 10.b})$$

N=1 for An(V) -- which exists only as AnO_2^+ -- as AnA ($z=1$), and
 N=2 for An(VI) -- which exists only as AnO_2^{2+} -- as AnA_2 ($z=2$); see also Sect. 4.4.
 In measuring concentrations, as in the SXRT method, the N numbers are close to the figures given but usually differ slightly from the whole numbers, e.g. 2.9, 3.1, etc.

Eq. (13.a) could as well be written

$$D_M^\circ = K_{\text{ex}} [\text{HA}]_{\text{org}}^N [\text{H}^+]^{-N} \quad (\text{Eq. 13.b})$$

These conditions have been widely used, first by (49CON/MCV), then by other researchers as is described in later sections on results of actinide hydrolysis measurements.

4.3.2 Other hydrophilic complexants (than OH)

The SXRT technique has been used to study actinide complexation by halides, sulfate, nitrate, etc; the results are discussed in Sect. 8, below. We represent all these anions by X. In the aqueous phase we have to consider the formation of a series of complexes MX^{z-1} , MX_2^{z-2} , MX_3^{z-3} , etc, all being hydrophilic; even the neutral complex MX_z is assumed not to be extracted.³

Analogous to eq. (8.a) we define a stability constant

$$\beta_x = [\text{MX}_x^{z-x}] [\text{M}^{z+}]^{-1} [\text{X}^-]^{-x} \quad (\text{Eq. 15})$$

Then

$$[\text{M}_{\text{tot}}]_{\text{org}} = [\text{MA}_z]_{\text{org}} = K_{\text{ex}} [\text{HA}]_{\text{org}}^z [\text{H}^+]^{-z} \quad (\text{Eq. 16.a})$$

and

$$[\text{M}_{\text{tot}}]_{\text{aq}} = [\text{M}^{z+}] \sum \beta_x [\text{X}^-]^x \quad (\text{Eq. 16.b})$$

and thus

$$D_M = K_{\text{ex}} [\text{HA}]_{\text{org}}^z [\text{H}^+]^{-z} / \sum \beta_x [\text{X}^-]^x \quad (\text{Eq. 17})$$

where the summation is taken up to maximum x-number. From this and eq. (13.a) one gets

$$D_M^\circ / D_M = \sum \beta_x [\text{X}^-]^x \quad (\text{Eq. 18})$$

where D_M° refers to the normalized extraction line. Thus, with eq. (18), measurement of the relative distribution ratio, D_M° / D_M , as a function of the concentration of the free ligand X yields a curve from which β_x is easily calculated. This technique has been extensively used to obtain the data in Sect. 8. Such studies are usually carried out at a pH where hydrolysis does not compete.

4.3.3 Hydrophilic complexes of the extractant; determination of [A]

(a) Formation of hydrophilic MA_n^{z-n} complexes

Eqns. 6 and 14 are the fundamental relations used in the "TTA-method", but the straight line deduced from eq. (13) may in practice not be straight over the whole

³ This is, of course, not always true and must therefore be contested in each particular case. For some SX systems, it is desirable that the neutral inorganic complex is extracted, e.g. in industrial actinide separations. For example uranium was/is purified by extraction as the $\text{UO}_2(\text{NO}_3)_2(\text{TBP})_2$ complex. However, for the sake of simple arguments we assume here that MX_z is not extracted into the organic solvent.

investigated range of $[HA]_{org}$ and $[H^+]$, but curve (downward, in a plot of $\log D$ versus pH) at higher values of $[HA]_{org}$ and pH. This indicates that hydrophilic aqueous complexes of M^{z+} may have been formed, either with OH^- or with A^- . Many studies have shown that the formation of the uncharged complex MA_z occurs through a successive attachment of ligands to the central metal atom. This also seems probable for the actinide-TTA complexes. Consequently, such complexes cannot *a priori* be neglected.

Assuming that MA_z is formed in a stepwise manner (i.e. MA^{z-1} , MA^{z-2} , $MA_z(aq)$), the stability constants are defined by

$$\beta_n = [MA_n] / [M] [A]^n \quad (\text{Eq. 19})$$

and

$$[M_{tot}]_{aq} = [M] + [MA] + [MA_2] + \dots = [M]_{aq} \sum \beta_n [A]^n \quad (\text{Eq. 20.a})$$

The distribution constant for the uncharged complex MA_z between the two phases is given by

$$K_{DC} = [MA_z]_{org} / [MA_z] \quad (\text{Eq. 21})$$

(indexed DC for Distribution of Complex). Then

$$[MA_z]_{org} = K_{DC} \beta_z [M] [A]^z \quad (\text{Eq. 20.b})$$

and

$$D_M = K_{DC} \beta_N [A]^N / \sum \beta_n [A]^n \quad (\text{Eq. 20.c})$$

where the summation n is taken over all complexes up to the maximum number N of A -groups which can be bound to M ; arbitrarily one may assume that $N = z$ (this assumption usually holds at low concentrations of HA).

In the absence of hydrolysis or of significant concentrations of other hydrophilic complexes, the measurement of D_M as a function of the "free ligand concentration" $[A]$ should yield a straight line of slope z ($\beta_0=1$, all β_n 's $\neq 0$), from which the product $K_{DC} \beta_z$ is obtained. Alternatively, the extraction curve deviates from linearity (usually bending downwards) with increasing $[A]$. Eq. 20.c is equivalent to Eq. 6.c. With these equations one finds that

$$K_{ex} = K_{DC} \beta_z K_a^z K_{DR}^{-z} \quad (\text{Eq. 22})$$

This relation is useful in understanding extraction constants; see e.g. 92RYD/MUS/CHO.

Instead of the concentration constants used in this section, with their apparent limitations, thermodynamic relations may be preferred. However, this adds experimental labor. Tables 2 and 3 give literature values of K_n and K_{DC} for some metal TTA systems. As available data are few on actinides, as well as for TTA, some additional data are presented in Table 4, which may be used to estimate relevant actinide TTA constants.

(b) Determination of $[HA]_{org}$ and $[A^-]$

From the dissociation constant of HA given by

$$K_a = [H] [A] / [HA] \quad (\text{Eq. 23})$$

and the distribution constant defined by

$$K_{DR} = [HA]_{org} / [HA] \quad (\text{Eq. 24})$$

Table 2. Constants for formation of TTA metal ion complexes:Log K_n refers to the reaction $MA_n^{z-n+1} + A^- \leftrightarrow MA_n^{z-}$

Metal	Condition	Log K_1	Log K_2	Log K_3	Log K_4	References
Lu(III)	0.1 Na,HClO ₄	6.0	6.0	5.6		68SCH/AND
Zr(IV)	1 M HClO ₄	8.8				56ZIE/CON
Zr(IV)	1.0 Na,HClO ₄	11.0	10.9	10.4	10.0	67MEL/OZE/PES
Hf(IV)	1.0 Na,HClO ₄	10.6	10.8	10.0	10.0	62PES/AUG
U(IV)	2 M Na,HClO ₄ (*)	8.8 to 9.0				50BET/LEI
Np(IV)	0.2 M HClO ₄	9.14	9.05	8.92	8.73	Est. fr. 54SUL/HIN
Np(V)	?	2.89	2.59			72GRO/KEL
U(VI)	75% dioxan corr. →0	8.7	7.9			65ROS/GOL

*) varying $[H^+]$, $[HA]$ **Table 3. Distribution constants, K_{DC} , for some metal chelates (HA=TTA) at 25°C.**

Metal complex	log K_{DC}	μ M	$[HA]_{org}$	Org. phase	References
BeA ₂	2.58	1.0 [*] (Na, H)ClO ₄	0.1	chloroform	68RUD/SEV/LAN
YA ₃	2.70	0.1(Na, H)ClO ₄	0.1	"	68SCH
AmA ₃	1.80	0.1(Na, H)ClO ₄	0.1	"	68SCH

*) at 17-20°C

Table 4. Comparison with acetylacetonate complexes

Metal	Condition	Log K_1	Log K_2	Log K_3	Log K_4	References
Th(IV)	0	8.3	7.7	6.2	5.1	Recalculated
Th(IV)	0.1 Na,HClO ₄	7.7±0.2	7.2±0.15	5.9±0.1	4.95±0.05	53RYD
U(IV)	0.1 Na,HClO ₄	8.6±0.2	8.4±0.4	6.4±0.3	6.1±0.05	55RYD/RYP
Np(IV)	1.0 Na,HClO ₄	8.58±0.07	8.65±0.05	6.71±0.02	6.28±0.02	70LIL/STA
Pu(IV)	0.1 Na,HClO ₄	10.5±1.0	9.2±0.5	8.4±0.4	6.0±0.2	55RYD

(index DR for Distribution of Reagent), one calculates

$$[HA]_{org} = K_{DR} [HA_{tot}] / (1 + K_{DR} + K_a [H]^{-1}) \quad (\text{Eq. 25})$$

and the "free ligand concentration" of the extractant

$$[A^-] = K_a [H]^{-1} [HA_{tot}] / (1 + K_{DR} + K_a [H]^{-1}) \quad (\text{Eq. 26})$$

These equations are valid provided $[HA_{tot}]$ (i.e. the total concentration of A added) $\gg [M_{tot}]$, which is one of the principles of the SXRT technique, and at equal phase volumes (cf. 92RYD/MUS/CHO).

Table 5. Log K_1 for the TTA protonation reaction $H^+ + A^- = HA$ at 25°C
 $\log K_1 \equiv pK_a \equiv -\log K_a$.

Condition	Log K_1	Reference
2 M Na,HClO ₄	6.17	50REI/CAL
<0.1 Na ⁺	6.38	52COO/TAF
1 M Na,HClO ₄	6.53	62PES/PEN
→ 0	8.64±0.02	65ROS/GOL
0.1 Na,HClO ₄	6.2	68SCH/AND
1.0 Na,HClO ₄	6.20	68RUD/SEV/LAN
0.1	6.23	69KEL/SCH
0.1 Na,HClO ₄	6.46	77INO/TOC

Some literature values of K_a and K_{DR} are given in Tables 5 and 6. Recommended values for TTA in the benzene / 1M Na,HClO₄ system at 25°C are $pK_a = 6.20$ ($K_a = 6.3 \cdot 10^{-7}$) and $\log K_{DR} = 1.54$ ($K_{DR} = 35$). With the values for K_{DR} and K_a one finds for TTA that not until pH 6 does the dissociation of TTA in the aqueous phase affect its concentration in the organic phase (eq. 26); at pH 7 the correction is 15% and then increases rapidly with pH. Inserting the values recommended above for TTA, $K_a K_{DR}^{-1} = 1.8 \cdot 10^{-8}$ (log value -7.75).

Table 6. Distribution constants K_{DR} for TTA (=HA) at t 25°C.

$\log K_{DR}$	μ M (Na, H)ClO ₄	[HA] _{org}	Org. phase	References
1.69	0.6	0.5	benzene	51ZEB/ALT/HEU
1.76	0.6	1.1	"	"
1.88	0.6	2.1	"	"
1.62	0.1	<0.05	"	64WAK/OKI/OMO
1.46	1.0	0.01	"	67HAL
1.54	1.0	0.1	"	"
1.70	1.0	1.0	"	"
1.54	2.0	0.01	"	70FOU
1.23	2.0 NaClO ₄	0.2	"	72KAS/KER
1.84	0.1	?	chloroform	64SEK/DYR
1.64	1-2 HClO ₄	?	"	67HAL
1.92	2.0	0.2	"	72KAS/KER

4.3.4 Several hydrophilic M-complexes

In the presence of both hydrolytic species and hydrophilic An-TTA complexes,

$$[M_{tot}]_{aq} = [M] + [MOH] + [M(OH)_2] + \dots [MA] + [MA_2] + \dots \quad (\text{Eq. 27.a})$$

or

$$[M_{tot}]_{aq} = [M]_{aq} (1 + \sum \beta_p [OH]^p + \sum \beta_n [A^-]^n) \quad (\text{Eq. 27.b})$$

where the summations for the hydroxide complexes are taken from p=1 to P, and of the A-complexes over n=1 to N. The distribution ratio becomes

$$D_M = K_{DR} \beta_N [A]^N (1 + \sum \beta_p [OH]^p + \sum \beta_n [A]^n)^{-1} \quad (\text{Eq. 28})$$

[A] and [OH] both depends on pH (one could write eq. 28 in terms of [H] and $[HA]_{org}$, if preferable), and in the same manner. Formation of hydrophilic OH- or A-complexes would decrease D_M from the straight normalizing line of eq. (13), and it would not be possible to distinguish by equilibrium methods what complexes are being formed. Therefore, other methods, kinetic or so-called fingerprinting ones (spectrophotometric in suitable wavelength region, NMR, etc) must be called upon for support. However, from experiments with varying ratios of [OH]/[A] (e.g., by varying pH at constant [A], which latter is kept constant through adjusting the $[HA_{tot}]$ value), one may find a region where the OH complexes dominate or can be neglected (cf. e.g. 56RYD).

Complexes of different strength are formed for the different actinide valency states: the strength of the complexes usually decrease in the order $An(IV) \gg An(VI) \gg An(III) > An(V)$. Although, in principle, the A-complexes, which form chelates, should be stronger than the OH-complexes, it is also a question of free ligand concentration (of [A] or [OH]), which in turn depend of the K_w and K_a values.

From the data in Table 4 (and also, for comparison, using data for acetylaceton complexes in Table 6, which are rather similar to the TTA complexes) one can estimate the following log K_1 values: for Th(IV) 7.2, U(IV) 8.1, Np(IV) 9.0, Pu(IV) 9.9, and for U(VI) 7.0; 1M Na_2HClO_4 , at 25°C. We assume all the K_n values (n = 1 to 4) for an actinide to be about the same, and that the following constants are valid: $\beta_1 = 10^9$, $K_a = 6.3 \cdot 10^{-7}$, $K_{DR} = 35$, $K_{ex} = 10^6$, and choose $[HA]_{org} = 0.1$ (a common experimental condition). One then finds that at [H] = 1 M about 2% of $[M_{tot}]_{aq}$ is complexed by TTA. However, the value actually decreases with pH, because the extraction parameter K_{ex} increases much faster than the complexation parameter β . At low values of $[HA]_{org}$ (say <0.1 M) the correction may be neglected.

To make these calculations complete, also the higher complexes of MA_n in the aqueous phases should be considered. From theoretical reason and experimental experience, it is likely that $K_n > K_{n+1}$ but for simplicity we assume $\beta_n = K_1^n$ to be valid. One then finds that 50% of the metal in the aqueous phase may be complexed with TTA. Consequently, this problem cannot be neglected, i.e. *the experimental conditions of a straight line according to eqns. 13 and 14 must be very carefully controlled*. It is a serious limitation to the TTA-method that in most studies the β_n values are unknown; cf. 54SUL/HIN.

Also, it is necessary to take into account some deviations of the distribution constant for TTA at higher [HA] concentrations. This can be done by the equation

$$[A] = K_a K_{DR}^{-1} [H]^{-1} [HA]_{org} (1 - 0.24 [HA]_{org}^{0.48}) \quad (\text{Eq. 29})$$

where the last parenthesis is the activity correction factor for $[HA]_{org}$ (51KIN/REA). See also Sect. 4.6.1.

4.4 Adduct formation

Actinides are "hard metals" and form strong complexes with "hard acids" (58AHR/CHA/DAV): i.e. the metal ions form ionic bonds with oxygen anions, and additional bonds with oxygen donor atoms, until the maximum coordination number N is reached. This number depends on the metal atomic charge and size, and available space around the metal complex. This means that the neutral complex may contain more A-molecules than z, i.e. $N \geq z$. The general formula for an "adduct complex" may be written MA_zB_b , where B is any neutral "adduct" molecule with oxygen donor atoms, coordinating to the neutral metal complex; if B is the same as HA, the complex formed is a "self-adduct". The equilibrium constant for this addition, believed to occur in the organic phase, is abbreviated K_{add} . It is not easy to predict N, but rather easy to measure it. It was early found that actinide acetylacetonates form self-adducts of the type $MA_z(HA)_b$ in the organic phase -- thus U(VI) forms the adducts $UO_2A_2(HA)_{1-2}$ (55RYD). Later it has been shown that all neutral actinide-TTA complexes form adducts with TBP (e.g. $Am(TTA)_3(TBP)_{1-2}$ (67SEK/DYR)), dipyrindyl and other strong donor molecules (77SEK/HAS, 78STA/FRE), and it is likely that TTA itself form self-adducts in a similar manner, though rather weak

complexes. It has been suggested that the self-adducts are no "adducts" but higher "normal" ionpair-complexes, e.g. not $MA_z(HA)_b$ but H_bMA_{z+b} ; it is not possible to decide about this from equilibrium experiments alone.

No polymers (dimers, etc) of TTA have been observed in the organic phase.

4.5 Complexes between the metal and the ionic medium

SXRT experiments are usually carried out at constant ionic strength to avoid activity factor corrections, the preferred medium being $NaClO_4$ (usually at 2M to 0.1M concentrations). For $HA=TTA$, both the formation of Na^+ -TTA complexes and $M^{z+}-ClO_4$ complexes would add more terms to the equations above. Though such complexes have been much discussed, the support for their formation is meager and in actinide-TTA studies their existence is neglected; we therefore do not include them in our subsequent review.

4.6. Other considerations

Chemical concentrations can be replaced by activities in the equations above (with a different β_n values, etc; β_n values are commonly tabulated at different ionic strength, as in 64SIL/MAR, 71SIL/MAR, 79PER, 82HÖG). Similarly, K_{DC} depends both on the aqueous ionic strength (usually increasing by increasing salt concentration, "salting out") and the solute concentrations in the organic phase.

4.6.1 Activity factors

The measured distribution ratios, D_M , are always concentration ratios. By using constant ionic strength in the experiments, concentrations can be used, assuming that all activity factors are constant, still yielding true (stoichiometric or mixed) equilibrium constants.

There is no easy way to control activity factors in the organic phase. It is commonly assumed that the activity factor for the extracted MA_z is the same as that for the extractant HA, which activity factor can be obtained from measurements of its distribution between the two phases, D_{HA} , at various $[HA]_{org}$ values:

$$K_{DR} = \gamma_{HAorg} [HA]_{org} / \gamma_{HAaq} [HA]_{aq} = D_{HA} \gamma_{HAorg} / \gamma_{HAaq} \quad (\text{Eq. 30})$$

where K_{DR} refers to Distribution equilibrium constant of the Reagent (HA), and D_{HA} to the measured distribution of same reagent (HA). K_{DR} values are listed in 78STA/FRE.

For TTA in the benzene/0.1M HCl system, 51KIN/REA found $D_{HA} = 40$ up to $[HA]_{org} > 0.01M$, after which it strongly increased, which was interpreted as the ratio $\gamma_{HAorg} / \gamma_{HAaq}$ strongly decreased. Assuming $\gamma_{HAaq} = 1$, they found $\gamma_{HAorg} = 1 - 0.24 [HA]_{org}^{0.48}$; in this system, D_{HA} reaches about 55 at $[HA]_{org} = 1M$; see eq. (29).

Reas (acc. to 49CON/MCV) found that γ_{org} for $U(TTA)_4$ was the same as γ_{org} for TTA at various concentrations of TTA in benzene. Hence, it is commonly assumed that $\gamma_{MAz,org} = \gamma_{HAorg}$. This assumption seems not to have been contested (or tested) by later investigators, although it is fundamental in most SX-TTA-studies; therefore, both ionic strength and $[TTA]_{tot}$ must be kept constant in careful experiments. Even if the assumption seems believable, the interaction between the solvent benzene (as used in most of these cases) and TTA, and between the " C_6H_6 -TTA" and the complex $M(TTA)_z$, though not physically identical, may yield the same activity coefficient. However, a safer approach is

to choose a solvent (like CHCl_3), which interacts less with HTTA in the concentration range studied; some investigators have preferred this slightly different system. This problem should be noted in comparing β_n 's obtained by the SX-method and obtained by other methods, as e.g. potentiometry and spectrophotometry (these techniques may have other pitfalls).

4.6.2 Kinetics

The kinetics of solvent extraction is usually fast if the reactants themselves are in equilibrium in the system. Then, equilibration times of 30 minutes are more than enough. Slow kinetics occur in polymerization, hydrolysis, change of metal valency states (especially between -yl and non-yl states) and for some reagents, who exist in different isomeric forms (keto-enol for beta-diketones).

Special attention must be directed to TTA, which appears in 3 different forms: keto, enol and ketohydrate, besides the dissociated enolate ion. 51KIN/REA have shown that starting with TTA-hydrate in benzene, it takes >300 hours to reach complete equilibrium. However, in the water/benzene system equilibrium is rapidly (i.e. within 1 hour) established between the enol and keto-hydrate, which amount to >95% of total TTA; the remaining <5% is keto-form slowly reaching equilibrium. For rapid experiments, it is advisable to start with TTA in the organic phase, which has been pre-equilibrated with the aqueous phase.

5. EXPERIMENTAL ASPECTS OF THE SXRT TECHNIQUE

5.1 The distribution ratio

In practice, distribution ratios can be measured reliably only between 10^{-3} and 10^3 by radiometric technique, but many publications present ratios above 10^3 or below 10^{-3} . Measurements of $10^{-3} > D > 10^3$ are very sensitive to experimental errors, as entrainment of small droplets of the high activity phase in the bulk low activity phase. This problem is discussed e.g. in 69AND/AND/LIL. It can be avoided by efficient centrifugation of the samples from each phase before measurement. This leads to an important requirement for the experimental SX work: *Absolute phase purity is required. D-values strongly deviating from 1 should be scrutinized for the technique.*

Several techniques have been devised for achieving absolute phase purity for samples of the two phases ("phase purity" is not relevant during the mixing stage). Thus slow stirring in Lewis cells avoids formation of small droplets which may be entrained in the other phase. Watari et al. (82WAT/CUN/FRE) have devised a filter, which is permeable only for one (the aqueous or organic) of the phases. Rydberg et al. (70REI/Ryd, 88ALB/OHL/PER) has developed a device with a high speed liquid-flow centrifuge for efficient phase separation in connection with continuous measurement of distribution ratios in solvent extraction studies. In batch experiments, efficient centrifugation and cleanliness may suffice.

To maximize the accuracy in the D -measurements, the SX-system is commonly adjusted by changes in pH and $[\text{HA}]$ so that the D -value stays close to one, then the hazard from the above difficulty is minimized. However, as this requires that the $[\text{HA}]$ and pH values are varied in a set of experiments, the measured D_M -values must be *normalized* with respect to these changes in order to make them comparable; see eqns. 13 and 18. The normalization can be made either to constant given values of $\{\text{H}^+\}$ and/or $\{\text{HA}\}_{\text{org}}$, or to unit activities. Although activity factors may be included, the normalized (corrected) and the measured (uncorrected) D_M -values are stoichiometric.

The various actinide valency states have very different extraction properties: e.g. one valency state may preferably enter one phase and the other valency state the other phase, see Table 1. Thus if a small amount of Pu(IV), which is easily extracted, is formed in a mainly Pu(III) system, from which Pu(III) is poorly extracted, the measured D -value will not reflect the Pu(III) behavior. Therefore *the actinide oxidation state must be 100% controlled*; this is further discussed in Section 6.

An interesting aspect of the SX technique is that the formation of aqueous extractant complexes, MA_n^{z-n} , lowers the concentration of free metal in the aqueous phase. The free metal concentration and pH are the essential parameters in hydrolysis studies (eq. 11), because polynuclear hydrolysis complexes are only formed at "high" free metal ion concentrations (not shown in eq. 11). Therefore, the SXRT technique can be used for studies of complex formation and mononuclear hydrolysis studies at pH-values where macroscopic studies are complicated by formation of polynuclear hydrolysis species. This was demonstrated already in 1950 in a study of aqueous complexation of Th(IV) by acetylacetonone up to pH 6 without interference from Th-hydrolysis (50RYD.2), something that would be impossible by potentiometric methods, compare Sect. 9 (54SUL/HIN). This condition seems to be missed in numerous later publications, including important reviews like 92GRE/FUG/KON and 95SIL/BID/RAN; cf. Sect. 7.1.

5.2. Radiometric technique

In Table 7 we list the actinide isotopes most commonly used for radiotracer work. Before using a radiotracer, its radiochemical purity must be verified: the radioactive "signals" should only come from isotopes of the element in the proper chemical state. Many simple detection methods are available for $\beta\gamma$ counting, like GM-detectors, Na(I) detectors, etc. However, nowadays liquid scintillation seems to be the preferred technique both for $\beta\gamma$ and for α emitting radionuclides. For $\beta\gamma$ counting, self-absorption, backscattering etc must be controlled (95CHO/LIL/RYP); if done systematically, $\phi_{org} = \phi_{aq}$ or $\phi_{org}/\phi_{aq} = \text{const.}$ (eqn. 4), and measurement of D_1 becomes a simple matter.

If liquid scintillation is used, the radiochemist must check that the detection efficiencies ϕ_{org} and ϕ_{aq} are known (or kept constant) throughout the whole range of parameter values. Often, this is taken for granted and not specified under "Experimental". It is, however, wrong to assume that this is trivial point. For example, using liquid scintillation with an extractant and/or solvent with strong *quenching properties* (like TTA and benzene), the detection efficiency may vary with several of the parameters (pH, [HA], etc). Thus; if the concentration of macroscopic components with quenching properties are varied and no corrections are made the distribution ratio will not correctly describe the chemical conditions (see e.g. 86ALB/RYP).

Table 7. Actinide isotopes suitable for radiotracer work

Nuclide	Half-life	Decay mode	Spec.act.(Bq/g)	Availability
²²⁷ Ac	21.8 y	$\beta\gamma$		Leaching U-ore
²³⁴ Th	24.1 d	$\beta\gamma$	$8.6 \cdot 10^{14}$	Milking U
²³¹ Pa	$3.3 \cdot 10^4$	α	$1.7 \cdot 10^9$	Leaching U-ore
²³³ Pa	27 d	$\beta\gamma$	$7.7 \cdot 10^{14}$	Irradiation Th
²³³ U	$1.6 \cdot 10^5$ y	α	$3.6 \cdot 10^8$	Irradiation Th
²³⁷ Np	$2.1 \cdot 10^6$ y	α	$2.6 \cdot 10^7$	Reproc. spent reactor fuel
²³⁸ Pu	88 y	α	$6.3 \cdot 10^{11}$	D:o
²⁴¹ Am	433 y	$\beta\gamma$	$1.3 \cdot 10^{11}$	D:o
²⁴² Cm	163 d	α	$1.2 \cdot 10^{14}$	D:o

At trace concentrations of multivalent ions (as e.g. Am^{3+}), a considerable fraction of the ions (sometimes >90%) may sorb on the walls of the experimental vessel, depending on ionic strength, pH, etc. (e.g. 83CAC/CHO.2). The sorption may occur with different kinetics, further complicating the trace measurements (e.g. 52RYD/RVD). Thus without controlling the details of the *sorption losses in both phases*, D may vary with pH in an uncontrolled way; again the extraction curve will deviate from the "true" one.

At metal trace concentrations, $[\text{M}_{\text{tot}}] \leq 10^{-6}$, *impurities* at this concentration level in the chemicals used may complex the metal to a degree which competes with the OH^- or A^- complexation (e.g. 66LIL/RVD). Such impurities are likely to ruin hydrolysis studies.

When high radioactivity concentrations of the radiotracer is used, the radioactive decay causes *radiation decomposition (radiolysis)* of the matrix (the water or the organic solvent). The radiolysis products are highly reactive radicals, which may interact with the central atoms as well as ligands, either oxidizing or reducing them. This fact should be born in mind, particularly in work with trace metal concentrations, so that the radiolysis does not interfere with the extraction process. Interfering radiolysis products may be controlled by special techniques, such as adding a "protective metal ion" (*scavengers*), which binds to the radiolysis products (e.g. 67LIL/RVD).

These examples serve as a reminder that the RTSX technique requires considerable care (as all techniques do, of course) in order to yield results of high quality. Unfortunately many authors using the SXRT technique inform too little about the technique *per se*. The reader is thus left only with the reputation of the researchers or of the laboratory of the work.

6. ACTINIDE REDOX EQUILIBRIA

The extraction constants for the An-TTA complexes vary considerably: according to Table 1, for An(III)-TTA $\log K_{\text{ex}}$ is about -8, for An(IV)-TTA being around +5 (except for Th), and for An(VI) about -2. Thus the extraction order is An(IV) \gg An(VI) \gg An(III). These conditions seem to be valid for all actinide - hard ligand type of complexes, and is used for industrial separation of actinides, e.g. in uranium production and in reprocessing of spent reactor fuel. (One of the first plutonium separation process was dubbed the REDOX-process for this reason.)

6.1 Effect of impure valency state

Radiotracer measurements (i.e. "counting") does not distinguish between various actinide valency states, as e.g. spectrophotometry does. As an example, in a solution of Pu(III) and Pu(IV), Pu(III) will have the same specific radioactivity (in Bq/mole) as Pu(IV), if the isotope exchange reactions have reached equilibrium (which is a requirement for the RT method). Thus, in a SX experiment

$$D_{\text{Pu}} = ([\text{Pu(III)}]_{\text{tot,org}} + [\text{Pu(IV)}]_{\text{tot,org}}) / ([\text{Pu(III)}]_{\text{tot,aq}} + [\text{Pu(IV)}]_{\text{tot,aq}}) \quad (\text{Eq. 31})$$

Because $D_{\text{Pu(III)}} \ll D_{\text{Pu(IV)}}$, any traces of Pu(III) formed by reduction of Pu(IV) (e.g. by radiolysis or organic impurities) will go into the aqueous phase; this will lower the D_{Pu} value, which could be interpreted as hydrolysis (or formation of hydrophilic complexes). And *vice versa*, in a Pu(III) solution any trace of Pu(IV) formed will go into the organic phase, raising the D_{Pu} value, which would obscure the effects of formation of hydrophilic complexes. Therefore, control of the oxidation state, depressing all formation of An(III) in

studies of An(IV) hydrolysis, and depressing all formation of An(IV) in studies of An(III) complexation is imperative when using the RTSX technique. For this purpose, holding reductants and oxidants are used. We briefly review a few such redox systems:

In Table 8 we calculate the effect of a small amount ("impurity") of Pu(VI) in a study of a Pu(IV) system: we assume $\log K_{\text{ex}}(\text{Pu4}) \approx 5.0$, and $\log K_{\text{ex}}(\text{Pu6}) \approx -2.0$ (cf. Table 1), for pH 0-3 and $[\text{TTA}]_{\text{org}} = 0.1 \text{ M}$. D_{correct} refers to the value which is obtained in absence of any Pu(VI) impurity, while D_{obs} is the actual value observed in the presence of the impurity (in modern jargon, a *virtual reality*). Hydrolysis is not included (though it is very strong for Pu(IV) at pH 3).

Table 8. Effect on observed distribution ratio for 1% and 5% Pu(VI) in Pu(IV)

pH	[Pu4] _{tot}	[Pu6] _{tot}	D_{Pu6}	D_{correct} (if only Pu(IV))	D_{obs} (virtuellt)
0	100	0		10	10
0	99	1	10^{-4}	10	9.0
0	95	5	10^{-4}	10	6.33
1	100	0		10^5	>> 1000
1	99	1	10^{-2}	10^5	99
1	95	5	10^{-2}	10^5	19
2	100	0		10^9	>>1000
2	99	1	1.0	10^9	199
2	95	5	1.0	10^9	39

From the Table it is seen that even small "impurities" (actinide in wrong valency state) can have a major effect on the measured D_M value. As K_{ex} is even smaller for Pu(III) than for Pu(IV) (Table 1), such an impurity in Pu(IV) can be even more disturbing.

Because of this *it is imperative in SX-studies of actinides which can appear in different valency states to ascertain that only one valency state exists in the system* both initially and at the end of the experiments, provided that no special technique is used to measure the concentration of several valency states simultaneously (cf. 55RYD).

6.2 The air-water system (neglecting complex formation):

Actinides have mostly been studied at ambient conditions, exposed to air at room (or 25°C) temperature. Under these conditions Ac(III), Th(IV), U(VI), Am(III), Cm(III), Bk(III) and Cf(III) are all stable, while the (IV)/(V) states of Pa and the (III)/(IV)/(V)/(VI) states of Np and Pu are unstable (i.e. no single oxidation state will dominate the solution).

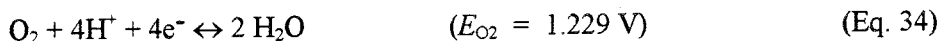
The ratio of $[\text{An(III)}]/[\text{An(IV)}]$ in air-water is obtained from the relation

$$\log R_{3/4} = \log[\text{An}^{3+}]/[\text{An}^{4+}] = (E_{\text{An}} - 1.229)/0.059 + \text{pH} - \frac{1}{4} \log p_{\text{O}_2} \quad (\text{Eq. 32})$$

where E_{An} is the normal (reduction) potential for the reaction



The reduction potentials are $E_{\text{U}} -0.631 \text{ V}$, $E_{\text{Np}} 0.155 \text{ V}$, and $E_{\text{Pu}} 0.982 \text{ V}$; the value 1.229 V refers to the reaction



Assuming trace concentrations of O_2 , $p_{O_2} = 10^{-8}$, then

$$\log R_{3/4}(U) = -29.5 + \text{pH}$$

$$\log R_{3/4}(\text{Np}) = -16.2 + \text{pH}$$

$$\log R_{3/4}(\text{Pu}) = -2.19 + \text{pH}$$

Thus, it should be easy to keep Pu(III) in anaerobic solutions at higher pH, while considerable care must be exercised with Np(III). It would be almost impossible to keep U(III), particularly at trace concentrations. This agrees with experimental experience. In Np and Pu solutions, where there is radiolysis, Np(III) and Pu(III) are slowly oxidized even in the absence of air.

6.3. Presence of a strong reductant

Strong reductants can reduce U, Np and Pu to the (III) or (IV) state, from which the U(III) and Np(III) are rapidly oxidized by air to the (IV) state, which is fairly stable (i.e. only slow oxidation) in acid solutions of U, Np and Pu. In order to preserve the Pu(III), or U(IV) state, a strong ("holding") reductant must be present, like Cr(II), SO_2 , N_2H_4 (hydrazine) or NH_2OH (hydroxyl amine); cf. e.g. 75AHR/LIL/RYP. Consider the An(III)/(IV) system in the presence of hydroxyl amine:

With the half cell



one gets

$$\log R_{3/4} = (E_{An} + 1.87)/0.059 + \log [NH_3OH^+] + 2\text{pH} \quad (\text{Eq. 36})$$

Assuming a large excess of reductant, putting $[NH_3OH^+] = 1$, one gets

$$\log R_{3/4}(U) = 21.0 + 2\text{pH},$$

$$\log R_{3/4}(\text{Np}) = 34.3 + 2\text{pH}$$

$$\log R_{3/4}(\text{Pu}) = 48.3 + 2\text{pH}.$$

Thus, with this reductant the An(III) species are stabilized and should be dominant. Radiolysis should have no effect.

6.4. Effect of hydrolysis of An(III) and An(IV)

The hydrolysis of An(III) and An(IV) shifts the redox equilibria in favor of the strongest complex former. Considering the first monomeric hydrolysis reaction, and using literature estimates for the β_p^* values

From literature	$\log^* \beta_1(\text{An3})$	$\log^* \beta_1(\text{An4})$
for U	-8.0	-1.5
for Np	-7.5	-1.0
for Pu	-7.0	-0.5
for Am	-6.5	0.0

using An3 for An(III), and An4 for An(IV), for easy reading. Abbreviating the ratio between *all* An(III) and *all* An(IV) species (for first hydrolysis step), $R_{3/4}(\text{all})$ (species), one obtains

$$R_{3/4}(all) = R_{3/4}(An) (1 + \beta_1(An3)[H^+]^{-1}) / (1 + \beta_1(An4)[H^+]^{-1}) \quad (\text{Eq. 37.a})$$

where $R_{3/4}(An)$ refers to the actinide redox systems in the tables above, Eq. (37.a) may be generalized to all p monomeric hydrolysis steps (though experimental values may lack for the higher β_p values)

$$R_{3/4}(all) = R_{3/4}(An) (1 + \Sigma \beta_1(An3)[H^+]^{-p}) / (1 + \Sigma \beta_1(An4)[H^+]^{-p}) \quad (\text{Eq. 37.b})$$

At pH 5, the ratio between the parenthesis, (...) / (...) is about 1/3,000 for U and 1/30,000 for Pu in the aerated system. Thus hydrolysis shifts the equilibrium in the system towards the +4 state.⁴ This means that hydrolysis worsens the problem of studying the hydrolysis of U(III), Np(III) and Pu(III). Thus, the conclusion reached at 6.1 that Pu(III) should be easy to study in the air-water system becomes less valid as pH increases. However, in the presence of a strong reductant (Sect. 6.2), $R_{3/4}$ is so large that hydrolysis will have little effect, and the +3 state should still dominate at all pH's.

6.5. Effect of other hydrophilic complexes

A large number of organic compounds have been used for extraction of actinides, and it is likely that substantial amounts of hydrophilic complexes are formed in the aqueous phase between these extractants and the actinide ions. However, only few such systems have been analyzed in such detail as to provide formation constants for the MA_n^{z-n} complexes; see Sect. 8.1 and 8.2.

In analyzing the effect of TTA complexation on the shift of redox equilibria for the actinides, it is most convenient to use the extraction constants K_{ex} , which are fairly well known (Table 1), rather than the hydrophilic complex formation constants β_n and distribution constants K_{DC} of the metal complexes, which are much less known (Tables 4 and 5). With eq. 6.a and referring $K_{ex}(An3)$ and $K_{ex}(An4)$ to the extraction constants by TTA (benzene) of An(III) and An(IV), respectively, the following data are used (mainly taken from 69DES/HUS/GUI and 77DUP/GUI:

for U	$\log K_{ex}(An3) = -8.2$	$\log K_{ex}(An4) = 5.0$
for Np	-8.1	5.1
for Pu	-8.0	5.2
for Am	-7.9	5.3

For simplicity we assume $[HA]_{org}=1$ (commonly it is ca. 0.1 M up to pH 7).

The ratio of total An(III) to total An(IV) (neglecting hydrolysis), $R_{3/4}$, is

$$R_{3/4}(all) = R_{3/4}(An) (1 + K_{ex}(An3)[HA]_{org}^3[H^+]^{-3}) / (1 + K_{ex}(An4)[HA]_{org}^4[H^+]^{-4}) \quad (\text{Eq. 37.c})$$

At $[HA]_{org}=1$, one gets for all the actinides U, Np and Pu that $R_{3/4}(all)$ (U, Np, Pu) $\gg 10^{-9}$ at pH's 1-5. Thus the TTA extraction system strongly shifts equilibrium in favor of the An(IV) state. However, using the $R_{3/4}$ values of Sect. 6.2 for the presence of a strong reductant as hydroxylamine, it should in principle still be possible to keep U, Np and Pu all in a stable An(III) systems.

⁴ Most complex formers, L, will do the same as the $An(IV)L_n$ complexes in general are more stable than the $An(III)L_n$ complexes. It is an important task in actinide separation to find deviations from this rule.

Similar estimates can be done for higher oxidation states of Np and Pu. Though they are of importance in nuclear waste analysis, they are outside the main purpose of this paper (to discuss the SXRT technique) and would add unnecessary length.

7. ACTINIDE HYDROLYSIS

7.1. The hexavalent state

Aerated U(VI) solutions are stable with no risk of reduction to lower valency states. The hydrolysis of U(VI) has been extensively studied (92GRE/FUG/KON) by potentiometric and spectrometric methods, and to some extent by solvent extraction (but not with TTA) and radiometric methods (as well as other metal detection methods). The SX studies are summarized in Table 9.1 (actually, no study qualifies in all respects for the title of this review).

55RYD applied the SX technique to the hydrolysis of U(VI) in 0.1 M NaHClO₄ using acetylacetone as extractant, and light absorption techniques for U determination. 60STA determined U(VI) hydrolysis by SX using benzoylacetone as extractant. In both these cases, the [U(VI)]_{tot} was too high (10 and 0.1 mM, respectively) to get acceptance by the OECD/NEA Data Bank review committee (92GRE/FUG/KON), because for the lack of considering polynuclear hydrolysis species. (This can, however, be debated as the reviewers in 92GRE/FUG/KON did not account for the actinide complexation by the extractant in the aqueous phase, which leads to a much lower free metal ion concentration, than formally calculated without this consideration; see Sect. 5.1). 54DAY/POW extracted U(VI) by TTA, but no investigation was made on hydrolysis (other metal-TTA extractions are listed e.g. in 64STA, 70DE/KHO/CHA and 77SEK/HAS). 83CAC/CHO determined the first hydrolysis constant of U(VI) (using ²³³U of high specific activity) by SX at several ionic strengths, and extrapolated to a thermodynamic hydrolysis constant; as extractant, they used dibenzoylmethane. Although the [U(VI)]_{tot} = 10⁻⁶ M this was not sufficiently low to allow neglecting polynuclear complexes, according to 92GRE/FUG/KON.

The OECD/NEA Data Bank gives selected (or preferred) equilibrium constants, presented in **bold letters** in Table 9. Despite the critics, the SX technique gives values for the U(VI) hydrolysis about ±1 order of magnitude of the selected value.

Only one SX study (85BID/TAN/CHA) has been made of the Np(VI) hydrolysis. Such studies require the presence of a strong oxidant, as e.g. persulfuric acid, which was assumed not to form any An(VI) complexes. In the presence of a strong oxidant, Np(V), which is less extractable, is not likely to interfere. The result, however, is not in accord with the selected constant for Np(VI), or with the U(VI) values.

7.2 The pentavalent state

Several actinides can be produced in water in the pentavalent state. Pa(V) is stable in aqueous solutions, but its hydrolysis is somewhat unclear. 65GUI only obtained mixed OH-TTA complexes in his comprehensive study. For the other actinides, other valency states form much stronger and more extractable complexes, so the equilibrium easily shifts away from the pentavalent state. The data are meager in 97NEA-TDB, but their selected formation constant is in the same range (considering the difficulties of studying this system due to the weak complexation and labile valency state) as that obtained by SXRT (85BID/TAN/CHA). It is believed that Np(V) and Pu(V) are important species in sea water, possibly as carbonate complexes.

Table 9. Hydrolysis of actinides studied by solvent extraction

9.1 Hexavalent actinides

Metal	Aq. conditions	Extractant	$\text{Log } \beta_1$	$\text{Log } \beta_2$	$\text{Log } \beta_3$	Reference
U(VI)	0.1 M NaClO ₄	acetylacetone	-4.20	-9.40		55RYD
U(VI)	0.1 M NaClO ₄	benzoylacetone	-5.0	-10.5	-17.1	60STA
U(VI)	0.0-1.0 NaClO ₄	dibenzoylmethane	-5.9-6.0			83CAC/CHO.2
U(VI)	0	Selected constants:	-5.2	<-10.3	-19.2	92GRE/FUG/KON
Np(VI)	0.2 M NaClO ₄		-9.60			85BID/TAN/CHA
Np(VI)	0	Selected constant: ⁵	-5.5			97NEA-TDB

9.2 Pentavalent actinides

Metal	Aq. conditions	Extractant	$\text{Log } \beta_1$	$\text{Log } \beta_2$	$\text{Log } \beta_3$	Reference
Pa(V)	1-3 Li,H ClO ₄	TTA	mixed			65GUI
Np(V)	0.2 M NaClO ₄	TTA/TOMA	-9.60			85BID/TAN/CHA
Np(V)	0	Selected constant: ⁵	<-11.4			97NEA-TDB

9.3 Tetravalent actinides

Metal	Aq. conditions	Extractant	$\text{Log } \beta_1$	$\text{Log } \beta_2$	$\text{Log } \beta_3$	Reference
Pa(IV)	1-3 Li,H ClO ₄	TTA	-0.14	-0.66	-2.43	65GUI
Np(IV)	1.0 Li,H ClO ₄	TTA	-0.5	-1.5		77DUP/GUI
Np(IV)	0	Selected constant: ⁵	-0.3			97NEA-TDB
Pu(IV)	1.0 Li,H ClO ₄	TTA,DBM,IPT/K ₂ Cr ₂ O ₇	-0.45	-0.75	-3.3	72&75MET/GUI
Pu(IV)	0.5 NO ₃ ⁻		-0.67			74SOL
Pu(IV)	0	Selected constant: ⁵	-0.5			97NEA-TDB

9.4 Trivalent actinides

Metal	Aq. conditions	Extractant	$\text{Log } \beta_1$	$\text{Log } \beta_2$	$\text{Log } \beta_3$	Ref.
Pu(III)	0.2 LiClO ₄	TTA, HyAm	-3.80			75HUB/HUS/GUI
Pu(III)	0	Selected constant: ⁵	-6.8			97NEA-TDB
Am(III)	0.1 H,LiClO ₄	TTA	-5.92			69DES/HUS/GUI
Am(III)	0.1 H,LiClO ₄	TTA	-5.3			73HUS/HUB/BRI
Am(III)	0.1 LiClO ₄	TTA	-5.30			76HUB/HUS/BRI
Am(III)	0.2 NaClO ₄	HDBM		-13.69	-12.87	82BID
Am(III)	1.0 NaClO ₄	TBP	-7.5			82LUN
Am(III)	0.70 NaCl	DBM	-7.54			83CAC/CHO
Am(III)	0.5 NaClO ₄	DNN	-6.8			87RAO/MAH/NAT
Am(III)	0	Selected constants: ⁵	-6.4±0.7	-14.1±0.6	-25.7±0.5	95SIL/BID/RAN
Cm(III)	0.1 H,LiClO ₄	TTA	-5.92			69DES/HUS/GUI
Cm(III)	0.1 H,LiClO ₄	TTA	-6.05			69GUI/FER
Cm(III)	0.1 H,LiClO ₄	TTA	-5.4			73HUS/HUB/BRI
Bk(III)	0.1 H,LiClO ₄	TTA	-5.66			69DES/HUS/GUI
Bk(III)	0.1 H,LiClO ₄	TTA	-5.1			73HUS/HUB/BRI
Cf(III)	0.1 H,LiClO ₄	TTA	-5.62			69DES/HUS/GUI
Cf(III)	0.1 H,LiClO ₄	TTA	-5.05			73HUS/HUB/BRI

HDBM = 1,3diphenyl 1,3 propanedione in benzene

HyAm = hydroxyl amine

TTA = thenoyl trifluoro acetone in benzene

TBP = tributyl phosphate 100%

DBM = dibenzoyl methane in benzene

DNN = dinonyl naphthalene sulphonic acid in benzene

ITP = isopropyl tropolone

⁵ Preliminary.

7.3 The tetravalent state

Although many studies of An(IV) complexation in aqueous solutions have been carried out by the SXRT technique, very few An(IV) hydrolysis studies have been made, probably due to experimental difficulties: (i) the An(IV) hydrolyses already in very acid solutions (pH 0-1), (ii) they very rapidly form polymeric species, and (iii) the An(IV) state easily disproportionates between other valency state (in "reactor grade" plutonium due to radiolysis)⁶. Nevertheless, the values obtained in Table 9.3 agree fairly well with the Selected constants (97NEA-TDB).

7.4 The trivalent state

For those actinides, which are chemically stable in their trivalent state, the determination of their hydrolysis constants is rather straight forward, with due consideration of the difficulties with trace concentrations and short half-lives.

Table 9.4 lists the results on An(III). While U(III) is very unstable in aqueous solutions, Np(III) is stable in 1M HClO₄ in absence of air; however, no SX study of its hydrolysis has been reported. Pu(III) is also stable in absence of air, but due to the strong tendency of Pu(IV) to form complexes (with OH⁻, TTA, etc; see Sect. 6) a holding reductant must be present like hydroxyl amine or hydrazine. The Pu(III) system investigated by 75HUB/HUS/GUI shows slow kinetics, the data are scattered, and the formation constant estimated is far from the Selected value by 97NEA-TDB. The large deviation can probably be attributed to experimental difficulties.

Table 10. Log*β₁ hydrolysis constants for Am(III) obtained by different techniques

Distribution RTSX	Electro- migration	El.migr. + RTSX	Potentiometr. titration	Solubility	Spectroscopy /technique
-5.48	-2.78	-6.69	-6.22	-7.26	-7.20 PAS
-2.57				≥-8.0	-7.06 PAS
-7.26				-6.0±0.8	-7.06 LIPAS
-4.86					-7.10 TRLIFS
-6.78					

PAS = PhotoAcoustic Spectrophotometry

LIPAS = Laser Induced PAS

TRLIFS = Time Resolved Laser Induced Fluorescence Spectrometry

Several groups have studied the hydrolysis of Am(III); from Table 9.4, the average value of the formation constant obtained by the SXRT method is *β₁ = -6.4±1.0, i.e. the same as recommended by 97NEA-TDB. It should be noted that Am(III) is perfectly stable under the experimental conditions. Table 10 compares results by the SXRT with those obtained by other techniques. The scatter of data within the SXRT technique is as bad as that between the different techniques; there is no single or simple explanation for this.

The French research group of Guillaumont has also determined hydrolysis constants for heavier trivalent actinides; see Table 9.4. The values seem reasonable, as compared to the other trivalent actinides.

⁶ This is only important for long-time experiments.

8. OTHER HYDROPHILIC ACTINIDE COMPLEXES STUDIED BY SXRT

8.1 Inorganic ligands

Table 11 surveys investigations by the SXRT technique of hydrophilic complexation of actinides. We will not review these systems here, as they will be covered in the forthcoming publication 97NEA-TDB.

8.2 Organic ligands

Over 700 solvent extractions systems for actinides are given in 77SEK/HAS; of these about 150 refer to extractions with TTA. Very few of these studies have been directed towards the determination of hydrophilic complexes, either with the extractants or with other hydrophilic organic compounds. This is obvious from Table 12, which covers all studies of hydrophilic complex formation between actinides and organic ligands found for solvent extraction. Some of these studies have been mentioned above in this review.

9. COMPARISON BETWEEN RTSX AND OTHER TECHNIQUES

The difference shown in Figure 1 for equilibrium constants determined by SX and by other techniques is claimed to be an effect of the use of tracer concentrations and not of the SX technique itself (77DUP/GUI); it is not quite clear how that can be so. Large (too large?) actinide(III) hydrolysis constants have been obtained both by Guillaumont and co-workers using SX (69DES/HUS/GUI, 69GUI/FER, 72HUS/HUB, 73HUS/HUB, 75HUB/HUS/GUI, 76HUB/HUS; see also 77DUP/GUI), and by researchers using electromigration (69MAR/KIK, 72SHA/STE, 74MEF/KRO), where the tracer scale usually refers to $\leq 10^{-5}$ M $[M_{\text{tot}}]$. However, many publications using the RTSX technique have yielded results in agreement with EMF, VIS and other techniques, including in hydrolysis studies. We discuss some of these important papers, which used TTA.

Sullivan and Hindman (54SUL/HIN) determined the sulfate complexation of Np(IV) in 2M Na(H)ClO₄ at 25°C by solvent extraction of the long-lived alpha-emitter ²³⁷Np ($[Np] \leq 10^{-4}$ M) by extraction with TTA ($\log[TTA]_{\text{org}} -0.7$ to -1.4 M) in benzene. They found that the complexation of Np(IV) by TTA in the aqueous phase became evident already at $[H^+] \leq 0.2$ M (i.e. the curve $\log D$ versus $[TTA]_{\text{tot}}$ began to deviate from the reference slope of -4). By measuring the reduction in the *relative (normalized) distribution ratio* as a function of the concentration of the hydrophilic ligand HSO₄⁻ (log conc. -3.1 to -0.8), they calculated the formation constants for NpHSO₄³⁺ and Np(HSO₄)₂²⁺. Activity factor corrections were introduced, also for HA and NpA₄ in the organic phase (51KIN/REA). By measuring the temperature dependency, the enthalpy and entropy of the complex reactions were obtained. These values are in good agreement with those of Patil and Ramakrishna (73PAT/RAM), using another SX system. The laboratories of Sullivan et al. and of Patil et al. both have a reputation of good experimental control.

Ermakov and Stary (67ERM/STA) determined aqueous complexation of Am, Cm, Cf and Fm in 0.5 M NH₄ClO₄ by lactic acid using solvent extraction with TTA (0.5 M) in benzene. The actinide concentrations were $1.8 \cdot 10^{-10}$ M ²⁴¹Am, $7.6 \cdot 10^{-12}$ M ²⁴⁴Cm, 10^{-19} M ²⁴⁶Cf and $2 \cdot 10^{-19}$ M ²⁵²Fm. The effect of lactic acid concentration (0.1 to 0.05 M) and pH (2.5 to 3) on the distribution ratio of the An(III) and, at the same time, of Eu(III), was studied, from which the formation constant β_3 for An(Lac)₃⁻ was calculated: $\log \beta_3(\text{Am}) \approx$

Table 11. Complexation of actinides by inorganic ligands studied by SXRT.

Complexation through hydrolysis is listed in Table 9, and by organic ligands in Table 14. References are given in year and first 3 letters of first and second author, see end of Table.

Actinide ion	F ⁻	Cl ⁻	Br ⁻ , I ⁻	NO ₃ ⁻	SO ₄ ²⁻	Others
Ac(III)		69SEKSAK 70RAOSHA	70RAOSHA	70RAOSHA	69SEKSAK 70RAOSHA	SCN ⁻ 68RAOSHA, 69SEKSAK Ox ²⁻ 69SEKSAK, 96CHOICHE H _x PO ₄ 70RAOSHA
Pa(IV)	65GUI	65GUI			65GUI	
Pa(V)	65GUI 66BUKFLE 67KOLRYA	65GUI 68GUIBOU			65GUI, 73LECGUI 74LUN	Ox ²⁻ 65GUI
U(IV)	54DAYPOW 69NOR	54DAYPOW 55DAYWIL 70LAHKNO		54DAYPOW 61WILKED 69RAOPAI 70LAHKNO	54DAYPOW 55DAYWIL 69RAOPAI	SCN ⁻ 55DAYWIL
U(VI)	69NOR 76PATRAM	70LAHKNO 88KHACHO	88KHACHO	70LAHKNO	58ALL 76PATRAM	H _x PO ₄ 57THA
Np(IV)	75PATRAM76 CHOUNR	66SHINAZ 71DANCHI 75PATRAM	75RAGRAM 79KUSGAN 80PATRAM	66SHINAZ 71DANCHI	73PATRAMa,b	Ox ²⁻ 79KUSGAN
Np(V)	79RAOGUD 84CHORAO 85INOTOC	71DANCHI 79RAOGUD 80PATRAM 95NECFAN	79RAOGUD	71DANCHI 79RAOGUD 80PATRAM	79RAOGUD 80PATRAM 85INOTOC	NO ₂ ⁻ , SCN ⁻ , IO ₃ ⁻ 79RAOGUD NO ₂ ⁻ , SCN ⁻ 81PATRAM H _x PO ₄ 85INOTOC
Np(VI)	68AHRBRA 76PATRAM 84CHORAO	71DANCHI 78BEDFID		71DANCHI	76PATRAM	H _x PO ₄ 69MOS
Pu(III)				59SCHTIM		SCN ⁻ 65CHOKET
Pu(IV)	76BAGRAM 77BAGRAM 84NASCLE	66DANORL 76BAGRAM	66DANORL 75RAGRAM	49ZEBNEU 64LAXPAT 66DANORL 76BAGRAM 77BAGRAM	64LUC 73PATRAMa 73PATRAMb 76BAGRAM 77BAGRAM	Ox ²⁻ 79KUSGAN
Pu(VI)	76PATRAM 84CHORAO	65MAZSIV 78BEDFID		52HEIHIC 65GHOSWA 65MAZSIV	76PATRAM	H _x PO ₄ 69MOS
Am(III)	69AZILYL 76CHOUNR	62PEPMAS 64SEK 65SEK 71KHONAR 82FUKKAW	82FUKKAW	62PEPMAS 64BANPAT65 CHOSTR70L AHKNO71KH ONAR 73CHIDAN	52HEIHIC 64SEK 65GHOSWA 65SEK2 67CARCHO 67CARCHO2 68AZILYL 72MCDL	SCN ⁻ 64, 65SEK, 65CHOKET, 71KOHNAR, 72HARPET, 73CHIDAN, 74KHOMAT, 74KINCHO H _x PO ₄ 86RAOMAH 88RAOMAH 78RAOBAG 80KHOMAT

References to Table 11.

- 49ZEB/NEU E L Zebroski, F K Neumann, fr. 79CLE
 52HEI/HIC D L Heisig, T E Hicks, *USAEC Report UCRL-1664*, 1952
 54DAY/POW R A Day, R M Powers, *J. Am. Chem. Soc.* **76**(1954)3895
 55DAY/WIL/HAM R A Day, R N Wilhite, F D Hamilton, *J. Am. Chem. Soc.* **77**(1955)3180
 57THA B J Thamer, *J. Am. Chem. Soc.* **79**(1957)4298
 58ALL K A Allen, *J. Am. Chem. Soc.* **80**(1958)4133
 59SCH/TIM/VOL V B Schevchenko, V G Timoshev, A A Volkova, *Soviet J. At. Energy* **6**(1959)293
 61WIL/KED A S Wilson, W E Keder *J. Inorg. Nucl. Chem.* **18**(1961)259
 62PEP/MAS/HUC D F Peppard, G W Mason, I Hucher *J. Inorg. Nucl. Chem.* **24**(1962)881
 64BAN/PAT/SHA B M L Bansal, S K Patil, H D Sharma *J. Inorg. Nucl. Chem.* **26**(1964)993
 64LAX/PAT/SHA T S Laxminarayanan, S K Patil, H D Sharma, *J. Inorg. Nucl. Chem.* **26**(1964)1001
 64LUC M Lucas, *Radiochim. Acta* **3**(1964)126
 64SEK T Sekine *J. Inorg. Nucl. Chem.* **26**(1964)1463
 65CHO/KET G R Choppin, J Ketels *J. Inorg. Nucl. Chem.* **27**(1965)1335
 65CHO/STR G R Choppin, W F Strazik *Inorg. Chem.* **4**(1965)1250
 65GHO/SWA A S Gosh Mazumdar, C K Swaramakrishnan, *J. Inorg. Nucl. Chem.* **65**(1965)2423
 65GUI R Guillaumont, *Physico-Chimie du Protactinium*, CNRS, Paris 1966
 65MAZ/SIV A S Mazumdar Gosh, C K Sivaramakrishnan, *J. Inorg. Nucl. Chem.* **27**(1965)2423
 65SEK, 65SEK2 T Sekine, *Acta Chem. Scand.* **19**(1965)1435; *ibid.* 1469, 1519
 66BUK/FLE/HAL M N Bukhsh, J Flegenheimer, F M Hall, A G Maddock, C F deMiranda, *J. Inorg. Nucl. Chem.* **28**(1966)421
 66DAN/ORL/SCI P R Danesi, F Orlandini, G Scibona, *J. Inorg. Nucl. Chem.* **28**(1966)1047
 66SHI/NAZ I V Shilin, V K Nazarov, *Sovjet Radiochemistry* **8**(1966)474
 67CAR/CHO, 2 R G De Carvalho, G R Choppin *J. Inorg. Nucl. Chem.* **29**(1967)725; *ibid.* 737
 67SEK/DYR T Sekine, D Dyrssen, *J. Inorg. Nucl. Chem.* **29**(1967)1481
 67KOL/R YA/SCH R T Kolarich, V A Tyan, R P Schuman, *J. Inorg. Nucl. Chem.* **29**(1967)783
 67SEK/DYR, 2 T Sekine, D Dyrssen, *J. Inorg. Nucl. Chem.* **29**(1967)1457; *ibid.* 1481
 68AHR/BRA S Ahrland, L Brandt *Acta Chem. Scand.* **22**(1968)106
 68AZI/LYL/NAQ A Aziz, S J Lyle, S J Naqvi *J. Inorg. Nucl. Chem.* **30**(1968)1013
 68GUI/BOU/MUX R Guillaumont, G Bouissieres, R Muxart, *Actinides Review* **1**(1968)135
 68RAO/SHA/MAT C L Dao, C J Shahani, K A Mathew, *Inorg. Nucl. Chem. Letters* **4**(1968)655
 69AZI/LYL A Aziz, S J Lyle *J. Inorg. Nucl. Chem.* **31**(1969)3471
 69MOS A I Moskvina *Sovj. Radiochim.* **11**(1969)447
 69NOR B Norén, *Acta Chem. Scand.* **23**(1969)931
 69RAO/PAI C L Rao, S A Pai, *Radiochim. Acta.* **12**(1969)135
 69SEK/SAK T Sekine, M Sakairi, *Bull. Chem. Soc. Japan* **42**(1969)2712
 70LAH/KNO H Lahr, W Knoch, *Radiochim. Acta* **13**(1970)1
 70RAO/SHA/RAO V K Rao, C J Shahani, C L Rao, *Radiochim. Acta* **14**(1970)31
 71DAN/CHI/SCI P R Danesi, R Chiarizia, G Scibona, G D'Alessandro, *J. Inorg. Nucl. Chem.* **33**(1971)3503
 71KHO/NAR P K Khopkar, P Narayanankutty *J. Inorg. Nucl. Chem.* **33**(1971)495
 72HAR/PET H D Harmon, J R Peterson, W J McDowell, C F Coleman, *J. Inorg. Nucl. Chem.* **34**(1972)1381
 72MCD/COL W J McDowell, C F Coleman, *J. Inorg. Nucl. Chem.* **34**(1972)2837
 73CHI/DAN R Chiarizia, P R Danesi, G Scibona *J. Inorg. Nucl. Chem.* **35**(1973)3595
 73LEC/GUI/DEM M F LeCloarec, R Guillaumont, C F deMiranda, J C Franck, *Radiochim. Acta* **20**(1973)1
 73PAT/RAMa S K Patil, V V Ramakrishna, *J. Inorg. Nucl. Chem.* **35**(1973)3333
 73PAT/RAMb S K Patil, V V Ramakrishna, *Radiochim. Acta* **19**(1973)27
 74KHO/MAT P K Khopkar, J N Mathur *J. Inorg. Nucl. Chem.* **36**(1974)3819
 74KIN/CHO W F Kinard, G R Choppin, *J. Inorg. Nucl. Chem.* **36**(1974)1131
 74LUN R Lundqvist, *Diss. Chalmers Univ. Techn. Gothenburg* 1974
 75PAT/RAM S K Patil, V V Ramakrishna, *Inorg. Nucl. Chem. Letters* **11**(1975)421
 75RAG/RAM/PAT R Raghavan, V V Ramakrishna, S K Patil, *J. Inorg. Nucl. Chem.* **37**(1975)1540
 76BAG/RAM/PAT S W Bagawade, V V Ramakrishna, S K Patil, *J. Inorg. Nucl. Chem.* **38**(1976)1339
 76CHO/UNR G R Choppin, P J Unrein, P. 97 in *Transplutonium elements* (Eds. W Müller and R Lindner), North-Holland Publ. Co. 1976
 76PAT/RAM S K Patil, V V Ramakrishna, *J. Inorg. Nucl. Chem.* **38**(1976)1075.
 77BAG/RAM/PAT S V Bagawade, V V Ramakrishna, S K Patil, *Radiochem. Radioanal. Letters* **31-2**(1977)56
 78BED/FID L Bednarczyk, I Fidelis, *J. Radioanal. Letters* **45**(1978)325
 78RAO/BAG/RAM P R V Rao, S V Bagawade, V V Ramakrishna, S K Patil *J. Inorg. Nucl. Chem.* **40**(1978)123
 79CLE J M Cleveland, *The Chemistry of Plutonium*, Am. Nucl. Soc., La Grange, Ill., USA 1979
 79KUS/GAN/GUD K M Kusumakumari, S P Gandhe, N M Gudi, S V Bagawade, P R Vasudeva Rao, V V

79RAO/GUD/BAG	Ramakrishna, A Ramanujam, S K Patil, <i>Bhaba Atomic Res. Cent. Report</i> 1005, p. 33, 1979
80KHO/MAT	P R V Rao, N M Gudi, S V Bagawde, S K Patil, <i>J. Inorg. Nucl. Chem.</i> 41 (1979)235.
80PAT/RAM/GUD	P K Khopkar, J N Mathur <i>J. Inorg. Nucl. Chem.</i> 42 (1980)109
82FUK/KAW/MIT	S K Patil, V V Ramakrishna, N M Gudi, <i>Proc. Nucl. Chem. Radiochem. Symposium 1980</i>
84CHO/RAO	T Fukasawa, I Kawasuji, T Mitsugashira <i>Bull. Chem. Soc. Japan</i> 55 (1982)726
84NAS/CLE	G R Choppin, L F Rao, <i>Radiochim. Acta</i> 37 (1984)143
85INO/TOC	K L Nash, J M Cleveland, <i>Radiochim. Acta</i> 36 (1984)129
86RAO/MAH/NAT	Y Inoue, O Tochiyama, <i>Bull. Chem. Soc. Japan</i> 58 (1985)2228
88KHA/CHO	V K Rao, G R Mahajan, P R Natarajan <i>Radiochim. Acta</i> 40 (1986)145
88RAO/MAH/NAT	F I Khalili, G R Choppin, E N Rizkalla <i>Inorg. Chim. Acta</i> 143 (1988)131
95NEC/FAN/RUD	V K Rao, G R Mahajan, P R Natarajan <i>Lanthanide and Actinide Research</i> 2 (1988)347
96CHO/CHE	V Neck, Th. Fanhängel, G Rudolph, J I Kim <i>Radiochim. Acta</i> 69 (1995)39
	G R Choppin, J F Chen, <i>Radiochim. Acta</i> 74 (1996)105

5.71, and, simultaneously, $\log\beta_3(\text{Eu}) \approx 5.84$. The results agree with values obtained by other techniques: the potentiometrically determined $\log\beta_3(\text{Eu})$ on macro concentrations of Eu(III) is 5.88 at ionic strength $\mu = 2.0$ M (61CHO/CHO) and 5.70 at $\mu = 0.2$ M (65DEE/VER).

In a study of another aqueous system (at 1 M NaClO₄) by Lundquist, Lu and Svantesson (84LUN/LU/SVA), the following $\log\beta_3(\text{Am})$ values were obtained: 5.32 (TBP), 5.65 (HDEHP) and 5.30 (TTA), and for Eu 5.76 (HDEHP) and 5.80 (TTA). Though three different extraction systems were used (indicated by the extractant within parenthesis), all with metals at trace concentration, the results were in fairly good agreement with previous works. This shows that the RTSX technique yields constants independent of the solvent system (when carried out properly) and in agreement with results obtained by potentiometry on macro concentrations.

Albinsson and Rydberg studied complex formation of trace amounts of Am(III) (86ALB/RYP), and of trivalent lanthanides in 1 M NaClO₄ (89RYD/ALB), with acetyl-acetone in benzene. The systems turned out to be complicated, but stepwise formation constants, $\log K_n$, were obtained for 9 lanthanides. The results agreed well with data from Nakamura et al. (85NAK/IMU), who studied the same system with the TTA extractant (at $\mu = 0.1$ M), and with Grenthe and Fernelius (60GRE/FER) and Yoneda et al. (64YON/CHO/BEA), who studied the system potentiometrically on macro concentrations of the elements; the deviations for individual $\log K_n$ values were ≤ 0.5 log units, with a tendency for the RTSX constants of being smaller than the potentiometric values (i.e. opposite to Fig. 1). In this study difficulties could be overcome by (i) using an advanced technique (AKUFVE-LISOL) for accurately measuring low D-values, $\leq 10^{-4}$, (ii) by strictly adhering to the Nernst distribution law, taking account of several species in the organic phase, and (iii) using liquid scintillation and correcting for changes in ϕ_{org} and ϕ_{aq} .

Cacecci and Choppin determined the hydrolysis of Eu(III) and Am(III) in 0.7 M NaCl (83CAC/CHO). In (83CAC/CHO.2) they describe in detail the RTSX technique used, which is of general interest to the studies on actinide hydrolysis. Specific care was exercised to avoid errors caused by sorption and by dissolved impurities (like traces of CO₂), which may suffice to bind the trace actinide in unknown side reactions. Thus, the walls of the vessels were covered by an anti-sorption layer, the solutions were filtered through micropore filters, a hold-back complexing agent (diglycolate) was added (it forms a trace-U(VI)-"pool"), and the experiments were carried out in a protective atmosphere. The results on Am(III) hydrolysis were close to those obtained by potentiometric titration, from solubility studies with solid Am(OH)₃, and with time-resolved laser-induced fluorescence spectroscopy. However, the results have been criticized by (95SIL/BID/RAN) for lack of consideration of higher complexes; cf. Sect 5.1.

Table 12. Studies of hydrophilic complexation of actinides by organic ligands, using the SXRT technique.

Compiled mainly from 64SIL/MAR, 71SIL/MAR and 79PER; data mainly up to 1974; for full references see these publications.

Ligand	Actinide - valency state	Abbreviated reference ¹
acetic acid	U-6,Am-3, Am-6, Cm-3,Bk-3	60STA, 63GRE,69VOD/OBU/PUS, 70CHO/SCH, 70HAR
acetylacetone	Th-4, U-4, U-6,Np-4, Pu-4	50,53,55,60RYD, 59RYD/SUL, 70LIL/STA
azelaic acid	Th-4, U-4	70MER/KUM/SKO
benzohydroxamic acid	Pu-4	66BBAR/BAR/BIO
benzoylacetone	U-6	60STA
methoxy SA ethane	U-6	66STR/ZIE/SAN
salicylideneaminobenzene	U-6	66STR/ZIE/SAM
carbamide	Pu-4	71SHM/SOK/KIR
CDTA	Am-3	66STA
cinnamoyl phenyl hydroxylamine	Th-4	67ZHA/SUK/OST
citric acid	Pa-5, U-6,Am-3, Cm-3, Cf-3	62STA/BAL, 68GUI, 71GUI/BOU, 70ADI/KLO/NEW
cupferron	Th-4	53DYR, 54DYR, 60RYD
decanoic acid	U-6	73NAK/HIR/TAN
dibenzoylmethane	U-6	70GRO
dichloro hydroxiquinoline	Th-4,Cf-3	56DYR/DYR/JOH,60RYD, 69FEI/KEL
dichloroacetic acid	Th-4	50DAY/STO
EDTA	Pa-5, U-6	60STA,69SHI/KIK/OMO
glycine	Am-3, Cm-3	68TAN/CHO
HEDTA	Am-3, Cm-3	71ZAM/MER/DUY
hexafluoro acetylacetone	U-6	70GRO
hydroxy-naphtaquinone	Th-4	59ZOU/PES
hydroxyacetic acid	U-6,Am-3, Cm-3, Bk-3	62STA/BAL,63GRE, 72CHO/DEG
hydroxybutanoic acid	U-6	62STA/BAL
hydroxyethyl iminodiacetic acid	Am-3 Cm-3, Cf-3	71ERM/VOR/ZAI
hydroxyphenyl iminodiacetic acid	Am-3, Cm-3, Cf-3	71ERM/VOR/ZAI
hydroxyquinoline	Th-4	53DYR, 60RYD
isopropyl tropolone	U-6	62DYR
lactic acid	Am-3 Cm-3, Cf-3, Fm-3	67ERM/STA, 71AZI/LYL
naphthonyl trifluoroacetone	Ac-3, Am-3, Cm-3,Cf-3	69KEL/SCH
nitriolo triacetic acid	U-6,Am-3, Cm-3	63STA,66STA
nitroresol sulphonic acid	Th-4, U-6,Pu-4	71BER, 72BER
oxalic acid	Ac-3, U-6, Am-3, Cm-3	60STA,64SEK, 66STA 69/SEK/SAK, 70AZI/LYL
phenylbenzo hydroxamic acid	Th-4	67ZHA/OST/SUK
phenylmethyl APZ	Ac-3, U-6, Am-3, Cm-3, Cf-3	73BAC/KEL
phenylmethyl BPZ	Ac-3,Th-4,U-6,Pu-4,Am-3,Cm-3,Cf-3	66ZOL/CHM/PAL, 73BAC/KEL
phenylmethyl chloroAPZ	Am-3	73BAC/KEL
phenylmethyl trichloroAPZ	Am-3	73BAC/KEL
phenylmethyl trifluoroAPZ	Am-3	73BAC/KEL
salicylideneaminoethane	U-6	66STR/ZIE/SAM
salicylaldehyde	Th-4	60RYD
salicylic acid	Th-4, U-6	56HÖK
Schiff base	U-6	68ZIE/STR
tartaric acid	U-6, Pu-4,Am-3,Cm-3	63, 66STA, 68ORT, 70ADI/KLO/NEW, 72MAR/KLO/NEW
thenoyltrifluoroacetone	Pa-5?, Am-3,Cm-3, Cf-3	68RUD/SEV/LAN, 68DYA/KHL/SPI,69KEL/SCH
tiron	Th-4	69BOG/MUR/MAR
cinnamic acid	Th-4	56HÖK, 60RYD
trichloroacetic acid	Th-4	50DAY/STO
trifluorothenoxyacetone	Pa-5, Pu-3	54KEE/SUT ,65GUI,
trioctylamine	U-6	60SHE/SHM/NEN
tropolone	Th-4	55DYR, 60RYD

1) Reference abbreviations according to OECD/NEA Data Bank. Other abbreviations:

c, or cond, refers to conditional constant; m, or mixed, refers to either mixed hydroxy or acid ligand complexes

APZ acetylpyrazolone

BPZ benzoylpyrazolone

CDTA cyclohexylene dinitriolo tetraacetic acid

HEDTA hydroxyethyl ethylenediamine triacetic acid

SA salicylideneamino

There are quite a number of other studies by SXRT, which yield results very close to those obtained by other techniques (e.g. 70LIL/STA, 82BID, 90CEC/FRE). In general, they demonstrate that SX tracer experiments, when carried out with experimental care, yield equilibrium constants that are neither higher nor lower than values obtained by other techniques.

10. CONCLUSIONS

The SX technique may not always be the most simple method for studying actinide complexation, particularly hydrolysis, because of the inherent problems of trace concentrations and radioactivity measurements and the instability of the actinide valency states. However, if the technique is applied with optimal care, controlling both the radiometric and extraction conditions, it yields equilibrium constants in agreement with other techniques.

Hydrolysis constants obtained by the SXRT technique are not available for all trivalent actinides, particularly for those which are easily oxidized: U(III), Np(III) and Pu(III). It would require that the experiments are carried out in the presence of some very strong reductant (e.g., controlled electrolytically). Also, solvent extraction with a good extractant like TTA shifts the equilibrium towards An(IV). Therefore, for the trivalent actinides it seems at present possible only to investigate the hydrolysis of the stable ones and of Pu(III) by TTA extraction, and perhaps Np(III) but only with great difficulty, and probably not at all U(III).

There are rather few investigations on the hydrophilic complexation of the tetravalent actinides by the extractant TTA. Such studies would be helpful as a ground for further studies of the mononuclear hydrolysis of An(IV), which is rather little known. The SXRT technique is unique in its ability to work at low actinide concentrations. As the tetravalent state is rather stable in nature, and actinide solutions of extreme dilution may appear in nature (dissolved from nuclear waste repositories), this should be a desired research field.

Although quite a number of studies have been made on the hydrophilic complexation of actinides by organic ligands (Table 12), it is still to a large extent a virgin field (cf. also 77SEK/HAS, 92RYD/MUS/CHO). This is also true for the thermodynamics and kinetics of solvent extraction of inorganic actinide complexes. When the SXRT technique is used either where other techniques are too insensitive (for example, it is the only useful technique for studying the the heaviest very short-lived elements) or supplementary to other techniques, it is necessary to control the aqueous phase (i.e. formation of hydrophilic complexes with the extractant) to avoid erroneous conclusions.

11. REFERENCES

Compilations are given in **boldface**.

- 02MOR H Morse, *Z. physik. Chemie* **41**(1902)709
 38GRA/SEA D Grahame, G T Seaborg, *J. Am. Chem. Soc.* **60**(1938)2524.
 41KOL/SAN I M Kolthoff, E B Sandell, *J. Am. Chem. Soc.* **63**(1941)1906
 49CON/MCV R E Connick, W H McVey, *J. Am. Chem. Soc.* **71**(1949)3182
 49IRV/WIL H Irving, R J P Williams *J. Chem. Soc.* (1949)1841
 50BET/LEI R H Betts, R M Leigh, *Can. J. Research* **28B**(1950)514
 50DAY/STO R A Day, R W Stoughton, *J. Am. Chem. Soc.* **72**(1970)5662.
 50HAG F Hagemann, *J. Am. Chem. Soc.* **72**(1950)768
 50REI/CAL J C Reid, M Calvin, *J. Am. Chem. Soc.* **72**(1950)2948
 50RYD J. Rydberg, *Svensk Kem. Tidskr.* **62**(1950)179.
 51KIN/REA E. L King, W H Reas, *J. Am. Chem. Soc.* **73**(1951)1804, 1806
 51ZEB/ALT/HEU E L Zebrosky, W H Alter, F K Heumann *J. Am. Chem. Soc.* **73**(1951)5646.
 50RYD.2 J Rydberg, *Acta Chem. Scand.* **4**(1950)1503
 52COO/TAF E H Cook, R W Taft *J. Am. Chem. Soc.* **74**(1952)6103
 52MAR/CAL A E Martell, M Calvin, *Chemistry of Metal Chelate Compounds*. Prentice Hall, 1956.
 52RYD/RYD J Rydberg, B Rydberg, *Svensk Kem. Tidskr.* **64**(1952)199
 52WAG/STO W C Waggener, R W Stoughton, *J. Phys. Chem.* **56**(1952)1
 53 RYD J Rydberg, *Arkiv för kemi* **5**(1953)413.
 53LAR/TER E M Larsen, G Terry, *J. Am. Chem. Soc.* **75**(1953)1560.
 54DAY/POW R A Day, R M Powers, *J. Am. Chem. Soc.* **76**(1954)3895
 54SUL/HIN J C Sullivan, J C Hindman, *J. Am. Chem. Soc.* **76** (1954) 5931.
 55DAY/WIL/HAM R A Day, R N Wilhite, F D Hamilton, *J. Am. Chem. Soc.* **77**(1955) 3180.
 55RYD J Rydberg, *Arkiv för kemi* **9**(1955)81, 109
 55RYD/RYD J Rydberg, B Rydberg, *Arkiv för kemi* **9**(1955)95
 56DYR D Dyrssen, *Sv. Kem. Tidskr.* **68**(1956)212.
 56RYD J Rydberg, *Rec. Trav. Chim. Pays-Bas.* **T75**(1956)737
 56ZIE/CON A J Zielen, R E Connick, *J. Am. Chem. Soc.* **78**(1956)5785.
 58AHR/CHA/DAV S Ahrland, J Chatt, N R Davies *Quart. Rev. Chem. Soc.* **12**(1958)265
 60GRE/FER I Grenthe, W C Fernelius, *J. Am. Chem. Soc.* **82**(1960) 6285.
 60STA J Stary, *Coll. Czech. Chem. Comm.* **25**(1960)890
 61CHO/CHO G R Choppin, J A Chopporian, *J Inorg. Nucl. Chem.* **22** (1961)97.
 61POS/FOR A M Poskanzer, B M Foreman, *J. Inorg. Nucl. Chem.* **16**(1961)323
 61ROS/ROS F J C Rossotti, H Rossotti, *Determination of Stability Constants*, McGraw Hill 1961
 62PES/PEN V M Peshkova, Pen-An, *Russ. J. Inorg. Chem.* **7**(1962)765
 63STO K P Stolyarov, Vest. Leningrad Univ., *Ser Khim. Fiz.* **4**(1963)140
 64FOT/FRE S C Foti, E C Freiling, *Talanta* **11**(1964)385
 64SEK/DYR T Sekine, D Dyrssen, *J. Inorg. Nucl. Chem.* **26**(1964)1727
 64SIL/MAR L G Sillén, A E Martell, *Stability Constants of Metal-Ion Complexes*, Spec. Publ. No 17, The Chemical Society, London 1964
 64STA J Stary, *The solvent extraction of metal chelates*. Pergamon Press 1964
 64WAK/OKI/OMO T Wakahayashi, S Oki, T Omori, N Suzuki *J. Inorg. Nucl. Ch.* **26**(1964)2255
 64YON/CHO/BEA H Yoneda, G Choppin, J L Bear, J V Quagliano *Inorg. Chem.* **3**(1964)1642.
 65DEE/VER H Deelstra and F Verbeek, *Anal. Chem. Acta* **31**(1965)251.
 65GUI R Guillaumont, *Physico-Chimie du Protactinium*, CNRS, Paris 1966
 65ROS/GOL Rosenstreich, J L, Goldberg, D E, *Inorg. Chem.* **4**(1965)909
 65SEK T Sekine, *Acta Chem. Scand.* **19**(1965)1519
 65SEK2 T Sekine, *Acta Chem. Scand.* **19**(1965)1469
 66LIL/RYD J O Liljenzin, J Rydberg, in *Physico-Chimie du Protactinium*, C.N.R.S. Coll. Int. No 154), Paris 1966.
 67ERM/STA V A Ermakov, I Stary, *Sovjet Radiochem.* **9**(1967)195.
 67HAL J Hala, *J. Inorg. Nucl. Chem.* **29**(1967)1317
 67LIL/RYD J O Liljenzin, J Rydberg, in *Solvent Extraction Chemistry* (Eds. Dyrssen, Liljenzin and Rydberg), North-Holland Publ. Co. 1967.
 67MEL/OZE/PES N V Melchakova, G P Ozerova, V M Peshkova, *Russ. J. Inorg. Chem* **12**(1967)577
 67SEK/DYR T Sekine, D Dyrssen, *J. Inorg. Nucl. Chem.* **29**(1967)1457
 67SEK/DYR2 T Sekine, D Dyrssen, *J. Inorg. Nucl. Chem.* **29**(1967)1481
 67SCH H Schreck, Kernforschungszentrum Karlsruhe, *Rep. KFK 672*, 1967
 68RUD/SEV/LAN N P Rudenko, A I Sevastyanov, H G Lanskaya, *Zh. Neorg. Khim.* **13**(1968)1566
 68SCH H Schweizer, Kernforschungszentrum Karlsruhe, *Rep. KFK 766*, 1968
 68SCH/AND G K Schweitzer, M M Anderson, *J. Inorg. Nucl. Chem.* **30**(1968)1051

- 69AND/AND/LIL C Andersson, S O Andersson, J O Liljenzin, H Reinhardt, J Rydberg, *Acta Chem. Scand.* **23**(1969)2781
- 69DES/HUS/GUI B Desiré, M Hussonois, R Guillaumont, *Compt. Rend. Acad. Sci. Paris*, **269**(1969) 488 Ser. C.
- 69GUI/FER R Guillaumont, C F de Miranda, M Galin, *C R Acad. Sc. Paris*, **268**(1969)140
- 69KEL/SCH C Keller, H Schreck, *J. Inorg. Nucl. Chem.* **31**(1969)1121.
- 69MAR/KIK B Marin, T Kikindai, *C R Acad. Sci. Ser. C*, **286**(1969)1.
- 69MET/GUI H Metivier, R Guillaumont, *Radiochem. Radioanal. Letters* **1/3**(1969)209
- 69SEK/SAK T Sekine, M Sakairi, *Bull. Chem. Soc. Japan* **42**(1969)2712
- 70BEC M T Beck, *Chemistry of Complex Equilibria*, Van Nostrand Reinhold 1970
- 70DE/KHO/CHA A K De, S M Khopkar, R A Chalmers, *Solvent Extraction of Metals*, Van Nostrand Reinholds 1970.
- 70FOU K F Fouché *J. Inorg. Nucl. Chem.* **32**(1970)3369
- 70LIL/STA J O Liljenzin, J Stary, *J. Inorg. Nucl. Chem.* **32**(1970) 1357.
- 70REI/Ryd H Reinhardt, J Rydberg *Chemistry and Industry* **1970**, 488
- 71ERM/VOR/ZAI V A Ermakov, V V Vorobeva, A A Zaicev, G NYakolev *Radiokhimiya* **5**(1971)692
- 71SIL/MAR L G Sillén, A E Martell, *Stability Constants, Supplement No 1*, Special Publ. No 25, the Chemical Society, London 1971
- 72GRO/KEL J Gross, C Keller, *J. Inorg. Nucl. Chem.* **34**(1972)3209 (D. Dyrssen Diss. 1955?)
- 72HUS/HUB H Hussonois, S Huberty, L Aubin, R Guillaumont, G Boussieres, *Radiochem. Radioanal. Letters* **10/4**(1972)231.
- 72KAS/KER E F Kassierer, A S Kertes, *J. Inorg. Nucl. Chem.* **34**(1972)3221
- 72MET/GUI H Metivier, R Guillaumont, *Radiochem. Radioanal. Letters* **10/2**(1972)27
- 72SHA/STE A B Shalnets, A V Stepamov, *Sovjet Radiochemistry* **14**(1972)290.
- 73HUS/HUB/BRI M Hussonois, S Hubert, L Brillard, R Guillaumont, *Radiochem. Radioanal. Letters* **15/1**(1973)47
- 73PAT/RAM K Patil, V V Ramakrishna, *J. Inorg. Nucl. Chem.* **35** (1973)3333.
- 74 SOL A S Solovkin, *J. Radioanal. Chem.* **21**(1974)15
- 74LUN R Lundqvist, Diss. Chalmers Univ. Techn. Gothenburg 1974
- 74MEF/KRO M Mefod'eva, N N Krot, T V Afanaseva, A D Gel'man, *Izv. Acad. Nauk SSSR, Ser. Khim.* **19**(1974)2370 (2361?)
- 75AHR/LIL/Ryd S Ahrland, J O Liljenzin, J Rydberg, in *The Chemistry of the Actinides*, Pergamon Press, Oxford 1975.
- 75HUB/HUS/GUI S Hubert, M Hussonois, R Guillaumont, *J Inorg. Nucl. Chem.* **37**(1975)1255.
- 75MET/GUI H Metivier, R Guillaumont, *J. Inorg. Nucl. Chem.*, Suppl. **1976**, p.179.
- 76HUB/HUS/BRI S Hubert, M Hussonois, L Brillard, R Guillaumont, in *Transplutonium Elements* (Eds. W Muller, R Lindner), North-Holland Publ. Co. 1976, p.77.
- 77DUP/GUI J Duplessis, R Guilleaumont, *Radiochem. Radianal. Letters* **31/4** (1977)293.
- 77INO/TOC Y. Inoue, O. Tochiyama, *J. Inorg. Nucl. Chem.* **39**(1977)1443
- 77SEK/HAS T Sekine, Y Hasegawa *Solvent extraction chemistry*. Marcel Dekker, New York 1977, 209ff.
- 78STA/FRE J Stary, H Freiser, *Equilibrium Constants of Liquid-liquid Distribution Reactions. Part IV: Chelating agents*, IUPAC Chemical Data Series No. 18, Pergamon Press 1978.
- 79PER D D Perrin, *Stability constants of metal-ion complexes. Part B, Organic ligands*, IUPAC Chemical Data Series No 22, Pergamon Press 1979
- 80HAR/BUR/ALC F R Hartley, C Burgess, R Alcock, *Solution Equilibria*, Ellis Horwood/Wikey 1980
- 82BID G Bidoglio, *Radiochim. Radioanal. Letters* **53/1**(1982)45.
- 82HÖG E Högfeldt, *Stability constants of metal-ion complexes. Part A, Inorganic ligands*. IUPAC Chemical Data Series No 21, Pergamon Press 1982
- 82LUN R Lundqvist, *Acta Chem. Scand.* **A36**(1982)741
- 82WAT/CUN/FRE H. Watari, L. Cunningham, H. Freiser *Anal. Chem* **54**(1982)2390
- 83CAC/CHO M S Cacecci, G R Choppin, *Radiochemica Acta* **33**(1983) 101.
- 83CAC/CHO2 M S Cacecci, G Choppin, *Radiochimica Acta* **33**(1983)207.
- 84LUN/LU/SVA R Lundquist, J F Lu, I Svantesson, *Acta Chem. Scand.* **A38** (1984) 501.
- 84RYD/LIL/ALB J Rydberg, J O Liljenzin, Y Albinsson, *Am. Inst. Chem. Eng. Symp. series* **238**, **80**(1984)47
- 85BID/TAN/CHA G Bidoglio, G Tanet, A Chatt *Radiochim. Acta* **38**(1985)21
- 85NAK/IMU S Nakamura, H Imura, N Suzuki, *Inorg. Chim. Acta* **109** (1985)157; see also N Suzuki, S Nakamura, *ibid.* 243.
- 86AHR S Ahrland, Ch. 21 in 86KAT/SEA/MOR.
- 86ALB/Ryd Y Albinsson, J Rydberg, *J. Less-Common Metals*, **122** (1986)175.
- 86KAT/SEA/MOR J J Katz, G T Seaborg, L R Morse, *The Chemistry of the Actinide Elements*, Chapman and Hall London 1986

- 87RAO/RAM/NAT V K Rao, G R Mahajan, P R Natarajan *Inorg. Chim. Acta* **128**(1987)131
88ALB/OHL/PER Y Albinsson, L E Ohlson, H Persson *Appl. Rad. Isotopes* **39**(1988)113
88MEL/HAV/HÖG M Meloun, J Havel, E Högfeldt *Computation of Solution Equilibria*, Ellis Horwood /Wiley 1988
89RYD/ALB J Rydberg, Y Albinsson, *Solv. Extr. Ion Exch.* **7**(4) (1989) 577;
90CEC/FRE T Ceconie, H Freiser, *Anal. Chem.* **62**(1990) 622.
92GRE/FUG/KON I Grenthe, J Fuger, R J M Konings, R J Lemire, A B Muller, C Ngyen-Trung, H Wanner *Chemical Thermodynamics of Uranium*. North-Holland 1992
92RYD/MUS/CHO J Rydberg, C Musikas, G Choppin *Principles and Practices of Solvent Extraction*, Marcel Dekker, New York 1992.
93ADL/GUI J P Adloff, R Guillaumont *Fundamentals of Radiochemistry* CRC Press 1993
95CHO/LIL/RVD G Choppin, J O Liljenzin, J Rydberg, *Radiochemistry and Nuclear Chemistry*, Butterworth-Heinemann, Oxford 1995.
95SIL/BID/RAN R J Silva, G Bidoglio, M H Rand, P B Robouch, H Wanner, I Pugdomenech, *Chemical Thermodynamics of Americium*, Nort-Holland Elsevier 1995
96SHA/PAI/PRV D C Shallcross, R Paimin, L M Prvcic *Value adding through solvent extraction*. Proc. ISEC'96, Univ. of Melbourne, 1996
97NEA-TDB NEA/TDB, *Chemical Thermodynamics of Np and Pu*; to be published

List of SKB reports

Annual Reports

1977-78

TR 121

KBS Technical Reports 1 – 120

Summaries

Stockholm, May 1979

1979

TR 79-28

The KBS Annual Report 1979

KBS Technical Reports 79-01 – 79-27

Summaries

Stockholm, March 1980

1980

TR 80-26

The KBS Annual Report 1980

KBS Technical Reports 80-01 – 80-25

Summaries

Stockholm, March 1981

1981

TR 81-17

The KBS Annual Report 1981

KBS Technical Reports 81-01 – 81-16

Summaries

Stockholm, April 1982

1982

TR 82-28

The KBS Annual Report 1982

KBS Technical Reports 82-01 – 82-27

Summaries

Stockholm, July 1983

1983

TR 83-77

The KBS Annual Report 1983

KBS Technical Reports 83-01 – 83-76

Summaries

Stockholm, June 1984

1984

TR 85-01

Annual Research and Development Report 1984

Including Summaries of Technical Reports Issued during 1984. (Technical Reports 84-01 – 84-19)

Stockholm, June 1985

1985

TR 85-20

Annual Research and Development Report 1985

Including Summaries of Technical Reports Issued during 1985. (Technical Reports 85-01 – 85-19)

Stockholm, May 1986

1986

TR 86-31

SKB Annual Report 1986

Including Summaries of Technical Reports Issued during 1986

Stockholm, May 1987

1987

TR 87-33

SKB Annual Report 1987

Including Summaries of Technical Reports Issued during 1987

Stockholm, May 1988

1988

TR 88-32

SKB Annual Report 1988

Including Summaries of Technical Reports Issued during 1988

Stockholm, May 1989

1989

TR 89-40

SKB Annual Report 1989

Including Summaries of Technical Reports Issued during 1989

Stockholm, May 1990

1990

TR 90-46

SKB Annual Report 1990

Including Summaries of Technical Reports Issued during 1990

Stockholm, May 1991

1991

TR 91-64

SKB Annual Report 1991

Including Summaries of Technical Reports Issued during 1991

Stockholm, April 1992

1992

TR 92-46

SKB Annual Report 1992

Including Summaries of Technical Reports Issued during 1992

Stockholm, May 1993

1993

TR 93-34

SKB Annual Report 1993

Including Summaries of Technical Reports Issued during 1993

Stockholm, May 1994

1994

TR 94-33

SKB Annual Report 1994

Including Summaries of Technical Reports Issued during 1994.

Stockholm, May 1995

1995

TR 95-37

SKB Annual Report 1995

Including Summaries of Technical Reports Issued during 1995.

Stockholm, May 1996

List of SKB Technical Reports 1996

TR 96-01

Bacteria, colloids and organic carbon in groundwater at the Bangombé site in the Oklo area

Karsten Pedersen (editor)

Department of General and Marine Microbiology,
The Lundberg Institute, Göteborg University,
Göteborg, Sweden

February 1996

TR 96-02

Microbial analysis of the buffer/container experiment at AECL's Underground Research Laboratory

S Stroes-Gascoyne¹, K Pedersen², S Daumas³,
C J Hamon¹, S A Haveman¹, T L Delaney¹,
S Ekendahl², N Jahromi², J Arlinger², L Hallbeck²,
K Dekeyser³

¹ AECL, Whiteshell Laboratories, Pinawa, Manitoba,
Canada

² University of Göteborg, Department of General
and Marine Microbiology, Göteborg, Sweden

³ Guigues Recherche Appliquée en Microbiologie
(GRAM), Aix-en-Provence, France

1996

TR 96-03

Reduction of Tc (VII) and Np (V) in solution by ferrous iron. A laboratory study of homogeneous and heterogeneous redox processes

Daqing Cui, Trygve E Eriksen

Department of Chemistry, Nuclear Chemistry,
Royal Institute of Technology, Stockholm, Sweden

March 1996

TR 96-04

Revisiting Poços de Caldas. Application of the co-precipitation approach to establish realistic solubility limits for performance assessment

Jordi Bruno, Lara Duro, Salvador Jordana,
Esther Cera

QuantiSci, Barcelona, Spain

February 1996

TR 96-05

SR 95

Template for safety reports with descriptive
example

SKB

December 1995

TR 96-06

Äspö Hard Rock Laboratory Annual Report 1995

SKB

April 1996

TR 96-07

Criticality in a high level waste repository. A review of some important factors and an assessment of the lessons that can be learned from the Oklo reactors

Virginia M Oversby

VMO Konsult

June 1996

TR 96-08

A reappraisal of some Cigar Lake issues of importance to performance assessment

John Smellie¹, Fred Karlsson²

¹ Conterra AB

² SKB

July 1996

TR 96-09

The long-term stability of cement. Leaching tests

Ingemar Engkvist, Yngve Albinsson,

Wanda Johansson Engkvist

Chalmers University of Technology,

Göteborg, Sweden

June 1996

TR 96-10

Lake-tilting investigations in southern Sweden

Tore Pässe

Sveriges geologiska undersökning,

Göteborg, Sweden

April 1996

TR 96-11

Thermoelastic stress due to an instantaneous finite line heat source in an infinite medium

Johan Claesson, Göran Hellström
Depts. of Building Physics and Mathematical Physics, Lund University, Lund, Sweden
September 1995

TR 96-12

Temperature field due to time-dependent heat sources in a large rectangular grid

– Derivation of analytical solution

Johan Claesson, Thomas Probert
Depts. of Building Physics and Mathematical Physics, Lund University, Lund, Sweden
January 1996

TR 96-13

Thermoelastic stress due to a rectangular heat source in a semi-infinite medium

– Derivation of an analytical solution

Johan Claesson, Thomas Probert
Depts. of Building Physics and Mathematical Physics, Lund University, Lund, Sweden
May 1996

TR 96-14

Oklo: Des reacteurs nucleaires fossiles (Oklo: The fossil nuclear reactors).

Physics study (R Naudet, CEA)

– Translation of chapters 6, 13, and conclusions

V O Oversby
VMO Konsult
September 1996

TR 96-15

PLAN 96

Costs for management of the radioactive waste from nuclear power production

Swedish Nuclear Fuel and Waste Management Co
June 1996

TR 96-16

Diffusion of I^- , Cs^+ and Sr^{2+} in compacted bentonite

– Anion exclusion and surface diffusion

Trygve E Eriksen, Mats Jansson
Royal Institute of Technology, Department of Chemistry, Nuclear Chemistry, Stockholm
November 1996