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ACTINIDES IN AQUEOUS SOLUTION AND THEIR CORRELATION
WITH FUNDAMENTAL PROPERTIES

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60 Abstract : Stability constants of the fluoride complexes of the actinides in different oxidation states measured by potentiometric method using fluoride ion selective electrode have been presented. Procedure and precautions required to overcome certain difficulties particular to actinide ions have been discussed. Literature data from various sources have been compiled. In order to have a reasonable comparison the stability constant (β_1) values obtained in diverse ionic strength media are converted to thermodynamic stability constant, β_1^0 , using Davies equation (a modification of Debye-Huckel equation). A correlation of the β_1^0 values with the fundamental properties of the actinide ions using various models available in the literature has been attempted. A semiempirical relation recently developed by Brown, Sylva and Ellis (BSE equation) appears to be most suitable. Using the values of ionic radii and best available values of the stability constants of a large number of metal ions from recent compilations a comparative study of the various models or relations available in the literature has been tried. For metal ions in general, the best correlation is obtained with the BSE equation. In an attempt to accommodate the unusual trend in the stability constants of the tetravalent actinides a modification in a parameter of the BSE equation has been proposed. Good agreement between the theoretically calculated and experimentally determined values for actinides in different oxidation states is then obtained in most of the cases.

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STABILITY CONSTANTS OF THE FLUORIDE COMPLEXES OF ACTINIDES IN AQUEOUS SOLUTION AND THEIR CORRELATION WITH FUNDAMENTAL PROPERTIES

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1. INTRODUCTION

Reliable values of stability constants are necessary for a good understanding of the nature of the metal complexes formed under a wide variety of conditions that are encountered in diverse areas of science and technology. Martel and Motekaites have given [1] a brief account of the various technical and scientific fields requiring stability constant data involving metal ions and complexing agents. They emphasized the need of quantitative information on chemical reactions and equilibrium conditions in diverse fields starting from general chemical and biological systems to the industries involving agriculture, metallurgy, corrosion, detergents, electroplating, environmental sciences, geosciences, membrane technology, oceanography etc. The fluoride complexes of actinides is of much interest in the study of solution chemistry of actinides. Fluoride complexation has important application in separation technology involving solvent extraction, chromatography, ion exchange etc. and in various analytical methods. Fluoride ion is a powerful catalytic agent for corrosion and is often used as an aid to dissolve ceramic oxides. It is a very useful masking agent. Reliable stability constant data are required in geological and environmental modeling [2] of the actinide elements to take into consideration the effect of this strongly complexing agent widely distributed, often at a high level, in nature. Apart from such applied aspects there is a need for reliable equilibrium data for theoretical studies towards the understanding of the nature of chemical bonds. Being smallest anion known to form strong complexes with the actinide ions and also being devoid of d - orbitals in the valency shell easy to participate in covalent π bonding (metal to ligand), fluoride is unique among the complexing agents. Thus, Hefter had attempted to correlate the stability constant data then available in the literature with the assumption that the

interaction was predominantly electrostatic in nature leading to the formation of purely ionic complexes [3]. Turner et al [2] attempted a systematic classification of the metal ions based on the difference in the $\log \beta$ values of the fluoro- and chloro- complexes.

A critical review by Bond and Hefter [4] sponsored by IUPAC was devoted exclusively to the stability constants of the fluoride complexes in aqueous medium. It was observed that the most commonly used techniques were solubility measurements, liquid-liquid extraction, ion exchange, polarography and potentiometry (using metal ion or pH electrodes). The details of the procedures involved in these techniques are available in standard books [5,6] and research communications. After assessing the reliability of each measurement the available data were divided into four categories: recommended, tentative, doubtful and rejected. As regards actinide elements, except for Th(IV) the stability constants values of all other actinides were included either in tentative or in doubtful category.

Until the development of the fluoride ion selective electrode, the "ferri" method of Brosset and Orring [7,8] was most commonly used potentiometric method. It utilises the effect of fluoride ion on the potential of Fe(III)/Fe(II) redox couple. A large difference in the strength of Fe(III) fluoride complexes relative to Fe(II) provides a sensitive measure of fluoride concentration. Typically a differential potentiometric technique is employed [7,8,9]. However, it presents a somewhat tedious experimental problem requiring the precise measurement and control of Fe(III)/Fe(II) ratio. It cannot be used to investigate systems which can either oxidise Fe(II) [e.g. Np(VI) or Pu(VI)] or reduce Fe(III) [e.g. U(IV)]. Again, it cannot be used to determine the stability constant of the first fluoride complex of a species forming much stronger complex than the first Fe(III) complex i.e. where k_1 of $MF^{(a-1)+}$ is much higher than k_1 of FeF^{2+} . It is not so good for weak complexes ($k_1 < 10$) also. Ferri method could not be used for actinide fluoride systems because either the stability constants were too high or there was interference with the desired oxidation state. Most of these data, were, therefore, obtained by solvent extraction and ion exchange methods. Presence of organic degradation products in these procedures often caused serious interference with the desired oxidation states even in the presence of holding reagents. In case of plutonium it was very difficult to maintain a single oxidation state. That might be the reason why no stability constant data on Pu(III) fluoride complexes had been reported in the literature. As Fluoride-Ion Selective Electrode (F-ISE) is free from these disadvantages it was strongly recommended [4] as the best tool for studying the fluoride complexes in general and actinide ions in particular.

F-ISE was first introduced by Frant and Ross [10]. The electrode is used for the potentiometric determination of free F^- ion in the same manner as the glass electrode is used

for the determination of H^+ . Concentration rather than activities have invariably been used. In non-fluoride-buffered media the limit of detection is 10^{-6} M. But the electrode appears to exhibit a close to Nernstian response over a wide fluoride concentration range of 1 M to 10^{-9} M in presence of metal fluoride complexes [11,12]. The only major interference is from OH^- which is eliminated at $pH < 6$. Unlike glass electrode it is resistant to hydrofluoric acid. The electrode response is unaffected in the presence of solid suspensions. Thus F-ISE is highly sensitive, selective and sturdy. Above all, it does not interfere with the oxidation state of the species in solution. Use of F-ISE in the measurement of stability constants had been successfully demonstrated by several workers [11,13,14,15,16] to obtain data on thorium and uranium complexes.

We had undertaken a study on the fluoride complexes of actinides at various oxidation states and measured the stability constants of the fluoride complexes of U(VI), Np(VI), Pu(VI), Np(V), Th(IV), U(IV), Np(IV), Pu(IV) and Pu(III) in $NaClO_4/HClO_4$ media of 0.1M and 1.0M ionic strengths using F-ISE Potentiometric technique [17,18,19,20,21,22,23]. Generally a high acidity is maintained to suppress metal ion hydrolysis. It must be emphasized that appreciable liquid junction potential (E_j) exists in acidic solutions even at low acidic and high ionic strength medium. For example in 1 M $NaClO_4$ medium E_j was reported to be 0.3 to 2.6 mV over the range of 5×10^{-3} to 4×10^{-2} M $HClO_4$ [24,25]. As these measurements were in acidic media the equilibrium data on the HF system and the liquid junction potentials, E_j , were necessary to account for the amount of fluoride ion consumed by the hydrogen ions and for the evaluation of free hydrogen and free fluoride concentrations respectively. Hence this work was started with a study on the fluoride complexes of H^+ . This report summarises various aspects of the methodology used in this work, measures taken to overcome the difficulties encountered at different stages and an assessment of the reliability of the stability constant values vis a vis those obtained by various methods reported in the literature. Finally, an attempt has been made to correlate the experimental values of the stability constants with fundamental properties of the ions.

2. AREAS REQUIRING CAREFUL ATTENTION

While working with the actinide ions extreme care had to be taken for (1) maintaining the desired oxidation state, (2) prevention of hydrolysis and polymerisation, (3) measurement of liquid junction potential which varied after each addition of titrant in the titration procedure, (4) Reliability of the auxiliary data used for accounting fluoride ion combined with the hydrogen ion and (5) onset of precipitation during the titration.

2.1 Maintaining the desired oxidation state

It was necessary to choose a reliable method for oxidation or reduction to ensure complete conversion to the desired oxidation state and also maintaining it during the period of experiment. An inert atmosphere and a high acidity of the medium were used to prevent the oxidation of U(IV), Np(IV) and Pu(IV). Addition of an appreciable amount of fluoride immediately after the preparation helped in preventing disproportionation of Pu(IV). Generally any additional holding oxidant or reductant was not used. In the case of Pu(III), quinhydrone was used as chemical reductant to reduce plutonium to trivalent state quantitatively. An excess of quinhydrone was added to serve as holding reductant.

2.2 Prevention of hydrolysis and polymerisation

High acidity prevented hydrolysis and polymerisation, particularly in presence of fluoride ion which acted as a strong depolymerising agent. In our titration procedure we initially added some fluoride ions and allowed to stand for some time before taking the first reading. Addition of some fluoride before inserting the F-ISE was also necessary to prevent any leaching of fluoride ion from the membrane of the electrode (lanthanum fluoride single crystal) by the acidic solutions especially of the tetravalent actinides which form very strong complexes with fluoride ion.

2.3 Measurement of liquid junction potential

An accurate knowledge of the total H^+ concentration in the beginning (H_T) is an important input in the evaluation of the liquid junction potential and the amount of fluoride consumed by the fluoride complexing of hydrogen ion. The fluoride electrode was always calibrated using potential values measured in nearly neutral standard fluoride solutions. Before the determination of free fluoride ion concentration in the actinide solution in which fluoride had been added it was necessary to correct for the liquid junction potential (E_j). It was formed at the reference electrode - measure solution interface and was mainly due to highly mobile H^+ in the measure solution. Hence E_j changed with the changes in the concentration of H^+ . As mentioned above while studying actinide ions in aqueous medium acidity was often kept high to minimise hydrolysis and polymerisation and also in some cases to stabilise the oxidation state. Consequently, an appreciable extent of E_j existed which had to be evaluated. The situation was further complicated by the partial association of the H^+ ion with the F^- ion added as titrant (NaF solution) to produce less dissociated HF and HF_2^- leading to a decrease in free H^+ concentration and hence a change in the E_j values. This had to be taken into account in the calculation of free fluoride and the metal ion-fluoride complex formed. $[H^+]$ and E_j

values changed as fluoride ion was progressively added in the measure solution. Therefore, for each potential measurement using F-ISE, simultaneous measurement of free H^+ was necessary to enable the calculation of the corresponding E_j and the fraction of total fluoride bound in the protonated complexes. However, the commonly used pH electrode using a glass membrane could not be used for this purpose as HF reacted with the membrane. Pt-quinhydrone electrode is generally used in such a case. But quinhydrone interfered with the desired oxidation state in several cases. For example, the addition of quinhydrone resulted in the reduction of Np(VI), Pu(VI) and Pu(IV) or oxidation of U(IV) as expected from their redox potential data. Thus Pt-quinhydrone electrode also could not be used to measure the free hydrogen ion concentration in the systems. This problem was overcome by developing [19] an iterative procedure for computing the $[H^+]$ from the measured potential data of F-ISE. Once $[H^+]$ was thus computed it was possible to calculate the E_j from the known dependence of E_j on $[H^+]$ measured beforehand. The values of free $[H^+]$ and E_j thus determined were used for evaluating the free $[F^-]$. The principle of the iterative method is presented in Appendix-1.

2.4 Reliability of the auxiliary data used for accounting the F^- combined with hydrogen ion.

Account of fluoride combined with H^+ as HF and HF_2^- must be included in the mass balance of total fluoride. Values of the stability constants of HF and HF_2^- (δ_1 and δ_2 respectively) used in the calculation must be sufficiently reliable. Hence values of these constants pertaining to the appropriate solution medium were determined before taking up experiments with the metal ions.

2.5 Onset of precipitation during the titration

In case of tetravalent and trivalent actinides, it was observed that at a certain point of titration when a sufficient amount of fluoride was added, the potential reading became unstable with a steady drift to more positive potential. This was attributed to the onset of precipitation and the titration process was terminated when this point was reached. Only those electrode potential data collected much before the onset of this instability were included in the calculation of the stability constants. In case of trivalent actinides and lanthanides this criterion restricted the data collection up to a low \bar{n} (average number of ligand ions attached to a metal ion) and a low free fluoride concentration in equilibrium. Nevertheless, analysis of the data showed that even at a low \bar{n} appreciable quantity of higher complexes were present.

By and large we had followed the experimental procedure of Ahrland and Kulbarg[24].

They reported the study of the fluoride complexing of the hexavalent uranium using F-ISE and their values are regarded to be reliable. As U(VI) is not reduced by the quinhydrone it could be used for simultaneous measurement of $[H^+]$ while titrating with sodium fluoride solution for the measurement of stability constants of uranyl fluoride system. The free $[H^+]$ after each addition of fluoride was measured directly by using Pt-quinhydrone electrode and was compared with that obtained by using the iterative method. A good agreement indicated the reliability of the iterative method for calculating $[H^+]$ and the E_j values. The details of the entire procedure were worked out satisfactorily using U(VI)-fluoride system. It was then extended to other systems with particular attention that was necessary for each system. In all solutions metal ion concentrations were quantified by rigorous analytical procedures. Free H^+ in the metal perchlorate solutions were analysed by the pH titration after adding complexing buffer solution.

3. POTENTIOMETRIC MEASUREMENT USING FLUORIDE ION SELECTIVE ELECTRODE

Combination fluoride electrode from ORION Research Inc. (Model 96-09) coupled to a digital ion analyzer (ORION 901 or 940) was used for the potentiometric determination of free fluoride ion at equilibrium after mixing fluoride ion with metal ion in a constant ionic strength perchlorate medium. Sodium perchlorate solutions (containing small amount of NaCl) of appropriate ionic strength were used as external filling solution to serve as salt bridge between the solution under measurement and the reference Ag/AgCl electrode incorporated in the combination F-ISE. The external filling solution was replaced every day before starting the experiments. The cell arrangement used for the determination of fluoride ion may be represented as follows

Reference Electrode	Salt Bridge	Measure Solution	F-ISE	Reference Electrode
Ag,AgCl External	External Filling Solution containing NaCl/NaClO ₄ Solution Saturated with AgCl	M _T -Metal ion in desired oxidation State H _T - HClO ₄ solution F _T - NaF Solution NaClO ₄ added for desired ionic strength	LaF ₃ Crystal Membrane	Ag,AgCl Internal Reference Solution containing NaF and NaCl

M_T, F_T and H_T are the total concentrations of metal ion, fluoride ion and hydrogen ion

respectively comprising the measure solution.

In case of H-F, Th(IV)-F and U(VI)-F systems the free H^+ concentration also was determined experimentally using Pt-quinhydrone electrode while using the same external reference electrode of F-ISE. The measured potentials of the fluoride electrode, E_F , and the quinhydrone electrode, E_H , were related to the respective concentrations by the equations

$$E_F = E_F^0 - S \log [F^-] + E_j \quad \dots 1$$

$$E_H = E_H^0 + S \log [H^+] + E_j \quad \dots 2$$

where E_F^0 and E_H^0 were the cell constants measured in the separate experiments. As the ionic strength was maintained constant the activity coefficient terms were regarded to remain constant and were included in the cell constants. The values of 'S' the response slope (theoretically $2.303RT/F$) were obtained from the electrode calibration experiments using standard solutions. E_j , the liquid junction potential at the interface of the measure solution and the bridge solution (i.e. the external filling solution of F-ISE), had to be evaluated. The experiments for the determination of stability constants were performed in the form of a titration by weight method. Weighed amounts of the fluoride solution were added in small drops from a weight burette the tip of which was drawn to a capillary. The weights were converted to volumes using density of the solution during calculation. Fluoride containing solutions were handled always in plastic labware. From the titration data and the measured potentials the concentrations of free H^+ , free F^- and the average number of fluoride attached to the metal ion (formation function or \bar{n}) were determined. These were then used for the computation of the concentration stability constants of the metal fluoride complexes using equilibrium relations. The details are given in [19].

4. METHODS OF CALCULATION

In the present study the concentration stability constants of the actinide fluoride complexes were evaluated from the measured equilibrium free fluoride concentration, $[F^-]$, and the \bar{n} using equilibrium relations. Three different methods were used. The first one was a graphical method developed by King and Gallagher [26] and was based on linearisation of the Bjerrum's equation relating \bar{n} and free ligand concentration. As expected from its basic assumption this method was applicable to the systems in which the stepwise formation constants were widely separated. It was useful for hexavalent and tetravalent actinides [19,22] but unsuitable for trivalent plutonium [23]. The second method was based on

nonlinear least square fitting of \bar{n} and free $[F^-]$ to the Bjerrum's equation (Eqn. 3)

$$\bar{n} = \frac{\sum_1^N n \beta_n [F^-]^n}{1 + \sum_1^N \beta_n [F^-]^n} \quad \dots 3$$

The computer program written for this purpose was named 'BETA'. The third method was available in the literature as program, 'MINIQUAD' [27] for processing potentiometric data. It was based on least square fitting to mass balance equations by minimising the residuals of total concentrations of fluoride ion, metal ion and hydrogen ion. After the required modifications for processing our primary data the program was adapted for this work. The computer programs of all the three methods of calculation were run on an ND computer. A comparison of the results obtained by all the three methods was given in the paper on tetravalent actinides [22]. The stability constant data are generally given as overall concentration stability constants, β_n , representing the equilibria



$$\text{where } \beta_n = \frac{[MF_n^{(z-n)+}]}{[M^{z+}] [F^-]^n} \quad \dots 5$$

In acidic medium the equilibria are represented as reaction with hydrofluoric acid



and the corresponding stability constants are represented by β_n° ,

$$\text{where } \beta_n^\circ = \frac{[MF_n^{(z-n)+}] [H^+]^n}{[M^{z+}] [HF]^n} \quad \dots 7$$

These overall constants are related by the equation

$$\log \beta_n = \log \beta_n^\circ + n \log k_1(H^+) \quad \dots 8$$

and the stepwise stability constants k_n and k_n° are related by the equation

$$\log k_n = \log k_n^\circ + \log k_1(H^+) \quad \dots 9$$

where $k_1(H^+)$ is the stability constant of HF given by



$$\text{and } k_1(H^+) = \frac{[HF]}{[H^+] [F^-]} \quad \dots 11$$

The stability constants calculated from the concentration of equilibrium species using the above equations are known as stoichiometric or concentration stability constants. Generally

the experimental measurements are carried out in the relatively high ionic strength medium to keep the activity coefficient fairly constant. The free acidity that is necessary to be maintained in the aqueous medium to prevent hydrolysis of the actinide ions does not allow measurements to be made at low ionic strength. Most of the measurements reported in the literature were therefore obtained at high and various ionic strength media containing, generally, NaClO₄ and/or HClO₄ as the supporting electrolyte. It is not proper to make any comparison of these values unless they are converted to the values corresponding to the same medium of preferably zero ionic strength to obtain the so called thermodynamic stability constants.

The thermodynamic stability constants for which activities rather than concentrations of the species are required in the calculation need individual activity coefficients which are seldom available. Approximate values are often calculated using the classical Debye-Huckel Method for binary electrolytes with charges Z₁ and Z₂ in dilute solutions [28]. The mean activity coefficient, ν_{\pm} , is given by

$$\log \nu_{\pm} = \frac{-A |Z_1.Z_2| \mu^{\frac{1}{2}}}{1 + B a \mu^{\frac{1}{2}}} \quad \dots 12$$

where 'a' is the ion size parameter in angstrom unit and A and B are constants for a given temperature and dielectric constant which may be taken from the table in [29]. However, it is difficult to guess a suitable value of 'a' in solutions containing background salt since physical significance of the ion size parameter is uncertain in mixed electrolytes.

Activity coefficients are more often estimated by means of one of the extended forms of the Debye-Huckel equation

$$\log \nu_{\pm} = \frac{-A |Z_1.Z_2| \mu^{\frac{1}{2}}}{1 + B a \mu^{\frac{1}{2}}} + C \mu \quad \dots 13$$

where C depends on the charge type and interaction coefficient of the electrolyte [30]. Davies [31] fixed the values of the unknown parameters and proposed the following expression at 25°C

$$\log \nu_{\pm} = - A|Z_1.Z_2|(\mu^{\frac{1}{2}}/(1+\mu^{\frac{1}{2}})-0.3\mu)$$

This was found to give good agreement with measured values in dilute solutions [31]. For individual ionic activity coefficients in a mixed electrolyte $|Z_1.Z_2|$ is to be replaced by Z_i^2 .

If the measurements are made in several ionic strength media then the values of a and C can be obtained by a suitable fit. In the absence of such measured values in a series of solutions of different ionic strength thermodynamic stability constants are calculated from measurement in only one ionic strength medium i.e. from a single stoichiometric stability

constant. Results obtained in this way should be treated with caution. Nevertheless, in order to have a reasonable comparison, the literature values of β_1 have been converted to β_1^0 using the equation

$$\log \beta_1^0 = \log \beta_1 - A \Delta Z_i^2 (\mu^{\frac{1}{2}} / (1 + \mu^{\frac{1}{2}})) - 0.3\mu \quad \dots 14$$

where $\Delta Z_i^2 = \sum Z_i^2$ (products) - $\sum Z_i^2$ (reactants).

The value of the constant A was taken as 0.5115. Only those measurements made at a temperature $298 \pm 5^\circ\text{K}$ and ionic strength $\leq 1\text{M}$ were converted to β_1^0 for this comparison. The stability constants reported in the literature are presented in the Tables 1-4.

A list of abbreviations of the methods used is given in the Appendix 2. The stability constant values obtained by ion selective potentiometry in this laboratory are presented in Table 5. Formation functions and speciation plots showing the distribution of different species as a function of equilibrium free [F] in the medium are presented in figs. 1-11.

5. STABILITY CONSTANTS OF THE FLUORIDE COMPLEXES OF ACTINIDES IN DIFFERENT OXIDATION STATES

5.1 Hexavalent and pentavalent actinides

The penta- and hexavalent states of the actinide cations are highly prone to hydrolysis and exist as oxygenated species such as MO_2^+ and MO_2^{2+} even in highly acidic medium. These oxidation states are exhibited by the actinides from Pa to Am except that the highest oxidation state of protactinium is Pa(V). The most stable oxidation state of Pa is Pa(V) though it is not certain whether the better formulation of the aqueous species is PaO_2^+ or $\text{PaO}(\text{OH})_2^+$ [32]. The pentavalent states of U, Pu, and Am are relatively stable in higher pH but have strong tendency to undergo disproportionation [33,34,35] which make their study in aqueous solution very difficult. Relatively stable oxidation states of uranium, neptunium and plutonium are U(VI), Np(V) and Pu(IV). However, hexavalent state of Np and Pu are fairly stable in perchloric acid medium to enable their studies. Thus it was possible to study hexavalent state of U, Np and Pu as UO_2^{2+} , NpO_2^{2+} and PuO_2^{2+} and pentavalent state of Np as NpO_2^+ . UO_2^{2+} -F⁻ system has been studied very extensively. In the work of Moore et al [36] and Tananaev et al [37] the ionic strength was not constant. The values from the spectrophotometric measurements [38,39] appear to be a little less than those obtained by other methods. There is a very good agreement between the results from potentiometric methods and from ditributive methods.

The stability constants of MO_2^{2+} -F⁻ (M = U, Np and Pu) were reported in [40] where

F-ISE was used. There appears to be some printing mistakes in the expression of \bar{n} (equation 3 in the paper). The constants for UO_2F^+ was also obtained by solvent extraction method. This was not possible for other two actinides due to their reduction to tetravalent state.

The values of NpO_2^{2+} and PuO_2^{2+} obtained by solvent extraction and cation exchange methods are likely to be uncertain as they were obtained from tracer distribution studies. Np(VI) and Pu(VI) were partially reduced to tetravalent state having large stability constant values unless a suitable holding oxidant was used. In [41] potassium dichromate was used as holding oxidant.

In [19] the stability constants of UO_2^{2+} , NpO_2^{2+} and PuO_2^{2+} fluoride complexes were measured using F-ISE. Equilibrium free H^+ concentration at each point of titration was measured or calculated for the correction of E_j . In case of UO_2^{2+} the free $[\text{H}^+]$ was directly measured using Pt-quinhydrone electrode. It was also calculated from the fluoride electrode potentials using an iterative procedure. In case of NpO_2^{2+} and PuO_2^{2+} it had to be obtained by iterative calculation only. Quinhydrone acted as a strong reducing agent and could not be used. The amount of F^- bound to H^+ was evaluated using the stability constants of HF and HF_2^- measured under the same conditions. The β_1 values of UO_2F^+ obtained by both the methods were in excellent agreement with the values obtained by Ahrlund et al [25] lending credence to the values of NpO_2^{2+} and PuO_2^{2+} obtained by the same procedure. The stability constant values given in [19] were obtained by using the method of calculation of King and Gallagher [26] only. The data were re-evaluated using three methods of calculations mentioned earlier. The values given in Table 5 are the averages of these values.

As shown in Fig. 11a the values of $\log \beta_1$, $\log \beta_2$ and $\log \beta_3$ follow the order $\text{U(VI)} > \text{Np(VI)} > \text{Pu(VI)}$ which is similar to that observed for hydrolysis constants [42] and for complexes with carboxylates [43]. The order was expected to be reverse considering the decreasing trend of the ionic radii. It has been argued that the effective ionic charges of oxometal ions are more than the formal value of +2 and follow a decreasing trend depending on how strongly the double bonded oxygen atoms are pulled towards the central metal ion. However the effective ionic charges calculated by Choppin and Rao [40] using extended Born equation is questionable as it involved an assumption (the input value of D_{eff}) which is almost tantamount to the final results. Following the study of Zachariassen [44] on the dependence of ionic radii of oxometal ions on the nature and number of ligands bound to them in the solid state, Brown and Sylva [45] assumed a similar dependence in the aqueous solution to define a maximum allowable ionic radius in the case of ligand bound in the primary hydration sphere of

the metal ion. Finally they expressed the dependence in terms of "apparent ionic radii" and formulated its relation with pK_a value of the ligand. It quantified the β_1 values and exhibited the observed decreasing trend. This approach seems to be more convincing. β_1^* for U(VI) obtained in our work agrees well with the average values obtained by different methods reported in the literature. As regards Np(VI) and Pu(VI) the only other potentiometric values [40], particularly in case of PuO_2^{2+} , appear to be slightly high.

The study on the fluoride complexes of actinides in pentavalent oxidation state is limited to Np and, to a lesser extent, to Pa. It is difficult to maintain this oxidation state in other actinides. In aqueous solution Np(V) is predominantly present as NpO_2^+ which does not undergo hydrolysis upto $\text{pH} \sim 8$ [46]. Fluoride complexing of NpO_2^+ can be studied in a low acidity (nearly neutral) medium using F-ISE. In [20] a value of 1.5 was obtained for $\log \beta_1$ by direct calculation using 1:1 complex whereas a titration procedure followed by graphical evaluation resulted in $\log \beta_1 = 1.76$. It was later revealed from the plot of titration data that the first two points at low $[\text{F}^-]$ deviated significantly from the fitted line. When these two points at low $[\text{F}^-]$ were omitted a much better fitting was obtained and the value of $\log \beta_1$ was 1.45 in close agreement with the directly measured value 1.5. Omission of the first two points were felt justified as the measurement of \bar{n} values below 0.005 may be considered as less reliable. In [47], the pentavalent state was shown to be unaffected during the solvent extraction procedure using dinonylnaphthalene sulphonic acid. Spectrophotometry of the two phases showed the presence of only Np(V). The results of [48] are close to this but the condition used are not specified. The stability constant value of NpO_2F measured in 1M NaClO_4 medium by solvent extraction method [40] is in good agreement with [20].

5.2 Tetravalent actinides

Among the tetravalent actinides, only Th(IV) exhibits a very stable oxidation state. Though Pa(IV) and Bk(IV) can be prepared in aqueous solution, they are very strong oxidants [32,49]. Am(IV) [50] and Cm(IV) [51] are also strongly oxidising and maintaining the oxidation state during the study is very difficult. U(IV), Np(IV), and Pu(IV) can be prepared and studied in aqueous solution with appropriate precautions to prevent oxidation by air or other oxidising agents. The tetravalent actinides are normally present in solution as M^{4+} and are strongly co-ordinated by solvent molecules. The hydrates formed in aqueous solution are strong acids with a tendency to dissociate off protons resulting in hydroxocomplexes which often condense into polynuclear complexes. It is therefore essential to maintain high acidity to prevent hydrolysis and polymerisation in aqueous

solution. High acidity is also necessary in case of Pu(IV) to avoid disproportionation. However, presence of a small amount of fluoride helps in the prevention of hydrolysis and polymerisation even at a low acidity [52]. Th(IV) is less susceptible to hydrolysis and can be studied at low acidity.

Generally, only mono- and sometimes mono- and bi-fluoride complexes could be studied using the solvent extraction methods. This was mainly due to the limitation of the maximum concentration of the reagent that can be used as extractant in the organic phase. Stability constants of higher complexes reported in the literature were obtained using potentiometric, nmr or solubility measurements. The stability constants of Th(IV)-Fluoride complexes measured by potentiometric and solvent extraction methods are in good agreement. They differ from the values of [53] using solubility and spectrophotometry in which proper conditions were not maintained. [54] measured the solubilities in 4M, 8M and 13M HNO₃ medium as a function of the concentration of HF. Dodgen and Rollefson [9] studied the potential of ferrous-ferric system as a function of the concentration of HF and Th⁴⁺. A steady change in potential was observed only after $\bar{n} = 1$ i.e. after ThF³⁺ had formed as expected from the high stability constant of the mono-fluoride complex. However, the data were interpreted assuming the existence of the species ThF³⁺, ThF₂²⁺ and ThF₃⁺. Values of stability constants reported in the literature were measured in nitrate or perchlorate media of various ionic strength. When those stability constants measured only in 1M perchlorate medium were considered the β_1^0 values of ThF³⁺ were in close agreement.

The first attempt of Day et al [55] for the determination of stability constants of the fluoride complexes of U(IV) yielded only approximate values of β_1 and β_2 . Afterwards, investigation on solubility of UF₄.2.5 H₂O as a function of fluoride concentration by Savage et al [56] gave the values of k_3^0 , k_4^0 , k_5^0 and k_6^0 . The values of potentiometric measurements of Kakihana and Ishiguro [15] and Choppin and Unrein [16] appear to be low. It is not mentioned whether the measured potentials were corrected for the change of liquid junction potential during the titrations.

Mostly cation exchange and solvent extraction methods have been used for Np(IV) and Pu(IV) fluoride complexes. The results of the measurement in [57] and [58] are much lower than the other values. This may be due to the complexation with nitrate ion from the nitric acid used for maintaining the ionic strength of the medium. In [59] the stability constants of Pu(IV) fluoride complexes were studied by solvent extraction method in the presence of NH₄VO₃ as the holding oxidant selected after a careful study of several other holding oxidants

and found to be most suitable for maintaining tetravalent state of plutonium. In case of Np(IV) no holding agent was used to maintain the oxidation state [60] and a lower value due to partial oxidation to hexavalent state during equilibration cannot be ruled out. These values were obtained in 2M ionic strength medium. [22] is the only potentiometric measurement. The β_1 value for Pu(IV) agrees well with most other measurements whereas for Np(IV) it is distinctly higher than others. It may be observed that the β_1 values of these tetravalent actinides follow the trend Th(IV) \ll U(IV) $>$ Np(IV) $>$ Pu(IV) and β_2 values follow Th(IV) $<$ U(IV) $>$ Np(IV) $<$ Pu(IV) where as β_3 and β_4 values follow an increasing trend (see Fig. 11a.) There are a few printing mistakes in [22]. The trend in the β_1 has been printed wrongly. The numbering of equation no.1 on page 298 is too close to the expression, 'natural' in third line from the bottom on page 305 should be 'neutral'. Other mistakes are, however, minor. As regards stepwise stability constants, K_n , the tetravalent actinides have some distinctive features. Apparently all tetravalent cations like Ce^{4+} , Zr^{4+} , Hf^{4+} etc. form very strong fluoride complexes as expected from their high charge and small ionic radii. However, β_1 values of these actinides ions are unusually high (much higher than expected from purely electrostatic interaction) particularly in case of U^{4+} . From a comparison of k_1 and k_2 it is evident that unlike other tetravalent cations the first fluoride complex is much more stable than the second. While k_1 values follow a decreasing trend from U to Pu, the reverse appears to be the case with k_2 values. The ratio k_1/k_2 is unusually high for U^{4+} and also follow the same decreasing trend. The values of k_3 in case of Th^{4+} , Np^{4+} , and Pu^{4+} are lower than k_4 . This is not expected from a simple electrostatic model of stepwise complex formation in aqueous solution. However, k_2 is higher than the mean value of k_3 and k_4 . The speciation plot show very little formation of the trifluoro complex after the formation of difluoro complex indicating almost simultaneous addition of two fluoride ions to form the tetrafluoro complex. It may be mentioned that the data included in the calculations in [22] were from titration points much before the onset of precipitation which, presumably, was indicated by the appearance of instability of the F-ISE potential.

5.3 Trivalent actinides

Among the earlier members of the actinides, Actinium exists as Ac(III) while trivalent Th and Pa do not exist in aqueous solution. U(III) and Np(III) are strong reducing agents in aqueous solution. U(III) undergoes slow oxidation even by water with evolution of hydrogen [34]. Higher actinides (except No) exhibit marked stabilization of the trivalent state. Among trivalent actinides Ac^{3+} , U^{3+} , Np^{3+} , Pu^{3+} , Am^{3+} , Cm^{3+} and Cf^{3+} are available in

amounts suitable for conventional chemical investigations. However study of U^{3+} and Np^{3+} in aqueous solution is rather difficult due to their susceptibility to oxidation. The stability constants of fluoride complexes reported in the literature are limited to Ac^{3+} , Am^{3+} , Cm^{3+} and Cf^{3+} . Mostly tracer distribution studies were used for these measurements. Electromigration method [61] was used for monofluoride complexes of Ac^{3+} and Am^{3+} . $\log \beta_3$ for Am^{3+} and Cm^{3+} obtained by solubility measurement [62] are distinctly low. The β_1 values of Am^{3+} and Cm^{3+} reported by Aziz and Lyle [63] are much higher than those reported by Choppin and Unrein [16]. The β_1 values of Am^{3+} to Cf^{3+} reported by Choppin et al [16] follow an expected increasing trend. The apprehension of a systematic negative bias [64] cannot be ruled out. The β_1 value of Am^{3+} measured by electromigration method is in agreement with [63]. The disagreement between the β_1 values of Aziz et al and Choppin et al should be resolved by independent measurement by some other suitable methods before applying any correction to the β_1 values of Cm^{3+} to Cf^{3+} reported in [16] as attempted by Fuger et al [64]. Our work [23a] on AmF^{2+} by distributive methods using two cation exchangers and two organic extractants gave β_1 values which agree well with each other and also with Choppin et al. (see foot note in Table-8). The stability constants of Pu^{3+} -fluoride complexes had not been reported in the literature before our work [23] probably due to the difficulty in maintaining the oxidation state. As fluoride forms a very strong complex with Pu(IV) a very small fraction of Pu present in tetravalent state would introduce a large error in the β values of Pu(III) and it must be ensured that Pu(IV) is almost totally absent. In [23] quinhydrone was used to reduce plutonium from higher oxidation state to the trivalent state and also to serve as a holding reductant. Nearly complete conversion of Pu(III) and absence of Pu(IV) and Pu(VI) were checked by potentiometry and spectrophotometry. The stepwise stability constant k_2 had large deviations and the average value was much less than k_3 . The speciation plot showed limited existence of difluoride. The same trend of k_2 less than k_3 is also observed in case of Am^{3+} [63].

6. CORRELATION OF THE EXPERIMENTAL VALUE OF THE FORMATION CONSTANTS WITH FUNDAMENTAL PROPERTIES OF THE IONS

Dimmock et al has reviewed various approaches to predicting stability constants [65]. Correlation of formation constants with fundamental properties of the metal ions and ligand elements had been attempted by numerous workers in various ways. Most of these were aimed at correlating the logarithm of the formation constant of the first mononuclear complex ($\log \beta_1$) with the ionic charge Z , and radius r , of the metal ion to obtain a linear

relation [66,67,68,69,3,71] and were found to be successful only for small ranges of complexes with ligands of closely related structure. These simple approaches are based on electrostatic interactions. Charge density of the metal ion which is proportional to (Z_+/r_+^2) was used by Palmer and ionic potential (Z_+/r_+) by Williams for linear correlations. Based on coulombic attraction between cation and anion linear relations of $\log \beta_1$ with $Z_+Z_-/(r_++r_-)$ where negative subscript refers to the anion and with Z_+^2/r_+ as expected from the equation for ion-dipole interaction were tried. Linear relation was observed with Z_+/r_{eff} where r_{eff} is the effective solution radius obtained by adding 0.85\AA (the radius of an oxygen atom in a water molecule) to the crystal radius of the cation [71]. Relatively recently, a more rigorous and versatile treatment attempted by Brown and Sylva [45,72] combined the properties of both metal ion (charge, radius and electronic structure) as well as the ligand (ionic charge, electronicity and pK_a of its parent acid) to formulate an empirical relation named as Brown-Sylva-Ellis equation (BSE equation) which was found to correlate the formation constants of the complexes of a large number of metal ions with various ligands. They also demonstrated that the equation was useful in predicting the formation constants of many metal ion-ligand complexes provided the required parameters in the equation are known. They considered the type of bonding orbitals available and the Slater screening constant [73] while extending and generalising the simple electrostatic model. This extended electrostatic model has been represented by

$$\log \beta_1 = \text{Int} + \text{Slp} [g_1(Z_+/r_+^2 + g_2)] \quad \dots 15$$

$$\text{where } g_1 = [1 + D + \epsilon_L^2 S] [Z_+ + 2], \quad \dots 16$$

$$g_2 = g(n) (Z_+ - 1) - 0.05d [(\gamma - 1) (\epsilon_L^4 - 3) - 1] [n - (3 + 2\gamma)]^2 [1 - \gamma Z_+] (1 - S) \quad \dots 17$$

and Int and Slp are the least-square intercept and slope of the linear equation for (1,1) complexes. D is equal to one if d-orbitals are available for bonding (otherwise $D=0$), S is 0 for the absence and 1 for the presence of s-electrons in the outermost shell of the ion (exhibiting the inert pair effects), $g(n)$ is a Slater function [73]. $g(n)$ is 1 when n, the principal quantum number, is greater than unity otherwise $g(n)$ is equal to 0. 'd' is the number of d-electrons in the outermost shell of the ions, γ is termed the ligand parameter and is 0 when the conjugate acids of the ligands are inorganic binary acids and 1 when they are inorganic oxyacids, ϵ_L is a new fundamental ligand property which with the corresponding metal property ϵ_M is a unifying concept called "electronicity" giving a measure of the freeness of the valence electrons. The presence of Z_+ in the expression for g_1 and g_2 indicates that $\log \beta_1$ is an indirect function of Z_+^2/r_+^2 (i.e. square of the ionic potential) and not of Z_+/r_+^2 as it may

appear at first glance.

An equation of this kind may be very useful for the estimation of formation constants of those complexes which cannot be easily measured experimentally. It was felt worthwhile to compare the experimentally determined stability constant values of the fluoride complexes of actinides at various oxidation states with those expected theoretically using these numerical relations.

Initially a comparative study was made to select the most reliable one from the relations mentioned above. Values of the stability constants of the monofluoro mononuclear complexes of various metal ions reported in the literature were collected mostly from the compilation of Bond and Hefter [4]. Generally values obtained in 1M and , in some cases in 0.5M ionic strength perchlorate medium (with NaClO_4 as the supporting electrolyte) were collected and converted to thermodynamic values using Davies equation (Equation 14 above). Values of Mn^{3+} and Sb^{3+} obtained in 2M perchlorate medium were included as these were the only relatively reliable values in the literature. While selecting the stability constant data from the various values in the compilation, preference was given in the order - Recommended > Tentative > Doubtful. Doubtful value was taken only when higher category was not available. Again, in each category, preference was given to potentiometric values particularly those obtained by ion selective potentiometry. Table 6 shows these values along with various parameters of the metal ion and the ligand. The values of ionic radii (based on the radius of $\text{O}^{2-}=1.40\text{\AA}$) were obtained from the compilation of Shannon [74]. The ϵ_L for fluoride was taken as zero.[45]

While using the BSE equation for correlation of the fluoride complexes of the metal ions an unusual feature was observed. As HF is an inorganic binary acid, the values of γ in all the three occurrences in the equation should be zero. However, when g_2 was calculated with all the γ values as zero, the elements containing electrons in 3d orbital fell on a separate line. When the value of γ in the second occurrence was taken as 1, as proposed by Brown et al [45] a good fit was obtained with all these elements except with Cu^{2+} and Mn^{3+} because of the uncertainty in the ionic radii due to Jahn-Teller distortion. The stability constant values of Be^{2+} and Al^{3+} are unusually high which may be due to certain extent of $p\pi-d\pi$ ligand to metal bonding resulting in shortening of bond as in silicon fluoride [75]. Al^{3+} fitted well with the linear relation when 5 coordinate radius (0.48\AA) was used instead of 6 coordinate radius (0.535\AA) for the monofluoro complex. The plot also shows the value of the stability constant of CeF^{2+} recommended by Bond and Hefter is actually a bit too high. The value

obtained by Walker and Choppin categorised as tentative [4] appears to be in order.

The basis of the various models that were considered for correlation and the X parameters taken for straight line fitting are presented in Table 7 along with the values of slope (Slp), intercept (Int) and correlation coefficients (Corr.Coeff.). Y-axis was the so called thermodynamic stability constant (β_1^0) converted from the reported values of β_1 as mentioned earlier. The plots are shown in Fig.12. It is evident from the corr.coeff. values that the BSE equation gives the best fit (separately shown in Fig.13.) and may be most suitable for predicting the unknown values of the stability constants.

7. CORRELATION OF THE STABILITY CONSTANTS OF THE FLUORIDE COMPLEXES OF THE ACTINIDES.

A perusal of the stability constants of the fluoride complexes of the actinides shows that the values are generally high compared to the stability constants of most other ions with the same formal charges. These values also exhibit some special trends in case of tetravalent and hexavalent actinides. Stability constant values increased sharply from Th^{4+} to U^{4+} and then decreased in Np^{4+} and Pu^{4+} . In case of hexavalent actinides it decreased from UO_2^{2+} to NpO_2^{2+} to PuO_2^{2+} . While the high values may be expected from a purely electrostatic consideration these particular trends cannot be explained by considering only charges and radii of the ions and it is necessary to invoke certain degree of covalent interaction based on the electronic configuration of these elements. Ahrlund, Hefter and Noren [76] studied the thermodynamics of the formation of fluoride complexes of Zr(IV), Hf(IV), Th(IV) and U(IV) by calorimetric measurements. The reaction with U(IV) is considerably more exothermic than the other reactions whereas entropy change is less favourable. The anomalously high value of the enthalpy change for the formation of UF^{3+} has been attributed to the formation of a much stronger bond in UF^{3+} than in other MF^{3+} complexes while opposite happens to be the case with the second complex.

BSE equation could correlate the above mentioned trend in tetravalent actinides provided we assume that one or two electrons are available in the 6d (outer most) orbital of the actinide ions in the beginning of the second inner transitional series. In the first few elements of the actinide series the energy levels of 5f, 6d and 7p orbitals are very close until about two electrons have been added when 5f level becomes definitely lower in energy and all those electrons are accommodated in 5f level only. Thus, while considering the fluoride complexes of tetravalent actinides the electronic configuration of Pa^{4+} , U^{4+} , Np^{4+} and Pu^{4+} were assumed to be $6d^1, 6d^2$, $5f^2 6d^1$ and $5f^4$ respectively. In fact, magnetic

susceptibility data on $\text{UF}_4\text{-ThF}_4$ and $\text{PuF}_4\text{-ThF}_4$ mixtures have been interpreted on the basis of $6d^2$ and $5f^4$ electronic configuration for uranium and plutonium tetrafluorides respectively [77,78]. With the ionic radii corresponding to coordination number six and the values of γ in the BSE equation as 1 in the first appearance and 0 in the second and third appearances the calculated stability constant values not only showed the trend but also showed close agreement with most of our experimental values as shown in Table 8. The γ values taken for calculating these stability constants as mentioned above are not as expected for a simple inorganic binary acid (i.e. zero in all the three appearances in the BSE equation) and demonstrate the unusual nature of complexing of fluoride ion with the actinides. The transitional elements were fitted to the equation with the γ values 0, 1 and 0. It may be noted that the second term in the expression of g_2 contains a term $(n-5)^2$ that makes its value progressively less negative reaching zero in 5d. It appears that in a continuing trend it becomes positive with 6d. In the beginning of the actinide series, one or two electrons may be available in 6d orbitals so that the second term in the expression of g_2 becomes positive. A good agreement between the calculated and the experimental values were obtained when the γ values in the BSE equation were taken as 1,0 and 0 respectively in the three occurrences. Thus the unusually high value of the stability constants of UF^{3+} and NpF^{3+} as well as the unusual trend in the monofluoride complexes of tetravalent actinides could be derived from the BSE equation. The unusual stability of the fluoride complexes of U(IV) and Np(IV) must have its origin in some kind of special bonding. Despite the stoichiometric resemblance in UF_4 and UCl_4 luminescence spectra show fewer and broader bands for UF_4 than for UCl_4 showing completely different interaction pattern of U(IV) with F^- [79]. It is worth examining whether there is a delocalisation of electron density from the orbitals of the metal ion to the vacant molecular or ligand orbital resulting in an increase in the bond energy [80].

The ligand donates electron density to the metal ion by overlapping its orbitals with metal s-function. As the 7s orbital is highly penetrating (with inner maxima), the portion of electron density which occupies these inner regions is particularly effective in shielding 5f or 6d electrons from the nucleus. This results in expansion of the electron density in these orbitals. The average distance between electrons increases and the inter electron repulsion parameters decreases. In such cases the metal-ligand σ bond is strengthened as long as the electrons are in the outer d and f orbitals that are not directed towards the ligands. This effect could be particularly manifested for the first step giving high values of k_1 . But, as more and more

electrons are filled up in the later elements in the series, electron density builds up in the orbitals directed towards the ligands and the metal-ligand σ bond becomes weaker due to repulsion. This may qualitatively explain the unusual trends in the β_1 values of actinide-fluoride complexes.

Theoretical calculations have revealed that even in fluoride complex of Ni^{2+} it is necessary to assume appreciable amount of π bonding [80]. The electron density that tends to be built up via σ system may be then dispersed through the π system. A synergetic effect can cause the two systems to help in augmenting the bonding ability of each other. Though F^- is more labile than O^{2-} the spectrum of UF_2^{2+} resembles the spectra of NpO_2^+ and PuO_2^{2+} more closely than does that of U^{4+} [81]. The species U(IV), Np(V) and Pu(VI) all have $5f^2$ electronic configuration. The blue shift (shift to a shorter wave length) of absorption peaks and also the appearance of small absorption peaks at about 430 and 500 nm when water molecules in the aquated U^{4+} ion is replaced by fluoride ion [81, 15] may perhaps be an indication of delocalisation of the metal electrons.

As regards pentavalent and hexavalent actinides, they are present as oxometal ions in aqueous solution. It is not possible to get correct values of g_1 and g_2 for the oxo-cations from their formal charges and ionic radii. Therefore, the value of the function $g_1(Z/r_1^2 + g_2)$ cannot be calculated directly. However, this could be estimated indirectly from reliable literature values of β_1 with various other ligands of known pK_a values. The values of $g_1(Z/r_1^2 + g_2)$ for the oxometal ions were calculated by substituting the values of $\log \beta_1^0$, Int. and Slp. of various ligands in the BSE equation (Equation 15). Int and Slp values of these ligands were taken from the work of Brown and Sylva [45] and β_1 values were collected from the latest compilations of data on actinides [82, 64]. These data are presented in Table 9. Reliable data on actinides are limited, particularly for plutonium. The plots of $g_1(Z/r_1^2 + g_2)$ vs pK_a of the ligand are shown in Fig. 14. The values of slope and intercept may then be used for calculating the values of the function for other ligands of known pK_a . However, when the usual value of the pK_a of HF was used the value of the function and hence the calculated values of β_1^0 of the fluoride complexes of oxometal ions were very low, although it showed the decreasing trend from U(VI) to Pu(VI).

Brown and Sylva [45] has shown that the slope of the BSE equation for a ligand is related to the pK_a value of its acid form by a straight line relation

$$\text{Slp} = 0.031(\pm 0.002) + 0.0078(\pm 0.0004) pK_a \quad \dots 18$$

where the number in parenthesis is the standard deviation. The correlation coefficient was 0.9840. The pK_a value of hydrofluoric acid was calculated from the slope (0.089) of the BSE equation for the fluoride complexes using the above equation. The value thus obtained was found to be 7.44 for hydrogen fluoride, which may possibly be a dimer as suggested by Brown and Sylva. Unpublished work in this laboratory on the existence of hydrogen fluoride oligomers also suggested the possibility of the dimer with pK_a value around 7.5 at zero ionic strength. When this value of pK_a was used the calculated values of β_1^0 followed the observed trend and also agreed well with our experimental values (except in case of PuO_2^{2+} for which reliable literature data for other ligands are limited) as shown in Table 10. Thus, a good correlation between the characteristics of the actinides ions and our experimental values of the stability constants of the fluoride complexes of actinides in different oxidation states was obtained when BSE equation was used except in the case of Th(IV) for which better agreement was obtained from Born equation and the stability constant calculated from BSE equation was much lower than the experimental value unless one electron is assumed to be transmitted to 6d or 5f orbitals via σ -system.

In conclusion it may be observed that the fluoride complexing of metal ions is influenced by the interaction with metal d-orbitals in different ways (with either strengthening or weakening of the bond) depending on their sizes and also whether these are vacant or occupied.

Three different situations can be envisaged:

1. Fluoride to metal π interaction as filled 2p orbitals of fluoride ion overlap with the vacant p or d orbitals of the metal ions (in the second and third period elements and in the metal ions in the beginning of the fourth period) giving higher stability.
2. Repulsion between filled 2p orbitals of fluoride and the electrons in the d orbitals of metals ions: This is reflected in the decrease of the value of g_2 in the BSE equation. The repulsion increases with increase in 'd' i.e. number of electrons in the d-orbitals and decreases with increase in 'n' i.e. increase in the size d-orbitals (more diffuse electron density) from 3d to 5d where the repulsion becomes nil with zero value of the factor $\{(n-3+2\gamma)\}^2$ in g_2 of the BSE equation.
3. Stronger covalent bonding due to delocalization of electron density to d or f orbitals followed by π interaction with fluoride ion. This situation is envisaged in case of higher valent actinides in which σ bond is formed by donating to the highly penetrating 7s orbital and 6d or 5f orbitals reach out to the ligand for π interaction.

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APPENDIX-1

THE ITERATIVE METHOD FOR THE EVALUATION OF LIQUID JUNCTION POTENTIAL, FREE FLUORIDE AND FREE HYDROGEN ION CONCENTRATION FROM THE MEASURED FLUORIDE ELECTRODE POTENTIAL.

The measured electrode potential, E_F , may be expressed as

$$E_F = E_F^0 - S \log[F] + E_J \quad \dots(1)$$

where $[F]$ is the concentration of free F ion, the approximate value of which was first calculated using equation(2) in which E_J was ignored.

$$[F] = \text{Antilog} - ((E_F - E_F^0)/S) \quad \dots(2)$$

This value was then used for computing the first approximate $[H^+]$ using equation (3)

$$[H^+] = H_T / (1 + \delta_1[F] + \delta_2[F]) \quad \dots(3)$$

where H_T is the total (combined and free) H^+ concentration, δ_1 and δ_2 are the stability constants of HF and HF_2^- respectively.

The E_J corresponding to this $[H^+]$ (as calculated from the known relation of E_J with $[H^+]$ measured beforehand) was then used in equation (4) to obtain a better approximation of $[F]$

$$[F] = \text{Antilog} - ((E_F - E_F^0 - E_J)/S) \quad \dots(4)$$

This was again used for the evaluation of a better value of $[H^+]$ using equation (3). This iterative procedure was continued until the difference between two successive E_J values was negligible and the correct values of $[H^+]$ and $[F]$ were obtained. The fluoride attached to the metal ion, F_M , was then obtained from the total fluoride, F_T , after subtracting the free F and the fluoride attached to hydrogen, F_H , using the following relation.

$$\begin{aligned} F_M &= F_T - [F] - F_H \\ &= F_T - [F] - H_T \cdot [F] \cdot (1 + \delta_1 + \delta_2[F]) / (1 + \delta_1[F] + \delta_2[F]^2) \end{aligned}$$

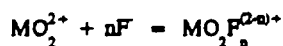
APPENDIX-2

LIST OF ABBREVIATIONS USED IN THE TABLES.

cal	calorimetry
cou	coulometry
cix	cation exchange
dis	distribution between two phases
emf	electromotive force, not specified
gl	glass electrode
ise	ion selective electrode
nmr	nuclear magnetic resonance
pol	polarography
pot	potentiometry
qh	quinhydrone electrode
red	emf with redox electrode
sol	solubility
sp	spectrophotometry
tp	electrical migration or transference numbers

Table-1.

Stability constants of the fluoride complexes of hexavalent actinides.

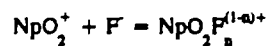


M	μ Medium	T	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	$\log \beta_4$	Method	Ref.	$\log \beta_1^0$	
UO_2^{2+}	4.0 (Na,H,ClO ₄)	298	4.90				qh	[83]	-	
	2.1 HClO ₄	298	4.48±0.06				cix	[84]	-	
	2.0 HClO ₄	298	4.69				dis	[41]	-	
	2.0 (NaClO ₄)	298	4.55				dis	[85]	-	
	1.04 HClO ₄	298	4.48±0.20				cix	[84]	4.89	
	1.0 (NaClO ₄)	293	4.54±0.05	7.89±0.05	10.46±0.05	11.81±0.10	qh	[86]	4.95	
	1.0 (NaClO ₄)	293	4.59±0.05	7.93±0.05	10.49±0.09	11.85±0.06	qh	[87]	5.00	
	1.0 (NaClO ₄)	298	4.54±0.01	7.98±0.01	10.42±0.01	11.89±0.03	qh	[25]	4.95	
	1.0 (NaClO ₄)	294	4.56±0.01	8.02±0.02	10.46±0.07	11.99±0.13	ise	[19]*	4.97	
	1.0 (NaClO ₄)	298	4.70±0.07				ise	[40]	5.11	
	1.0 (NaClO ₄)	298	4.52±0.10				dis	[40]	4.93	
	1.0 NaClO ₄	298	4.39				qh	[85]	4.80	
	1.0 NaCl	298	4.39	7.77	9.83		ise	[88]	4.80	
	0.65 NaClO ₄	298	4.12				sp	[38]	4.77	
	0.51 HClO ₄	298	4.47±0.11				cix	[84]	5.01	
	0.50 (NaClO ₄)	298	4.31				dis	[85]	4.85	
	0.25 (NaClO ₄)	298	4.49				dis	[85]	5.02	
	0.2 HClO ₄	298	4.50±0.08	7.48±0.09	10.44±0.10		cix	[84]	5.01	
	0.1 (NaClO ₄)	294	4.78±0.01	8.14±0.08	10.13±0.17	11.66±0.25	ise	[19]*	5.00	
	0.05 HClO ₄	298	4.86				dis	[85]	5.20	
	<0.01	293	4.78				sp	[39]	4.96	
	var	298	4.0±0.1	8.7±0.02			sol	[37]	-	
var HCl	298	4.32				aix	[36]	-		
NpO_2^{2+}	2.11 HClO ₄	298	5.26±0.03				cix	[89]	-	
	1.0 HClO ₄	298	4.25±0.05				dis	[41]	-	
	1.04 HClO ₄	298	5.16±0.03				cix	[89]	5.56	
	1.0 HClO ₄	294	3.88±0.15	7.01			dis	[90]	4.29	
	1.0 (NaClO ₄)	294	3.94±0.01	6.73±0.02	8.29±0.07		ise	[19]*	4.35	
	1.0 (NaClO ₄)	296	4.27±0.05				ise	[40]	4.68	
	1.0 (NaClO ₄)	296	3.77	6.92			cou	[91]	4.18	
	0.5 HClO ₄	296	3.89	6.79			cou	[91]	4.43	
	0.5 HClO ₄	298	4.04±0.01	7.0±0.01			red	[92]	4.58	
	0.4 HClO ₄	298	4.05±0.01	7.05±0.01			red	[92]	4.59	
	0.3 HClO ₄	298	4.06±0.01	7.05±0.01			red	[92]	4.60	
	0.2 HClO ₄	298	4.08±0.01	7.04±0.01			red	[92]	4.59	
	0.1 HClO ₄	298	4.12±0.01	7.01±0.01			red	[92]	4.55	
	0.1 (NaClO ₄)	294	4.15±0.08	7.08±0.09	9.83±0.10		ise	[19]*	4.58	
	PuO_2^{2+}	2.0 HClO ₄	298	5.13±0.05	10.08±0.08	14.91±0.13	19.20±0.19	cix	[93]	-
		2.0 HClO ₄	298	4.21				dis	[41]	-
1.0 (NaClO ₄)		296	4.22±0.07				ise	[40]	4.63	
1.0 HClO ₄		298	5.07±0.05	10.07±0.08	14.96±0.10	18.14±0.15	cix	[93]	5.48	
1.0 (NaClO ₄)		294	3.80±0.15	6.31±0.15	8.00±0.17		ise	[19]*	4.21	
0.1 (NaClO ₄)		294	4.05±0.10	6.88±0.12	9.05±0.17		ise	[19]*	4.48	

* Recalculated

Table-2

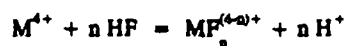
Stability constants of fluoride complexes of pentavalent actinides.



M	μ Medium	T	$\log \beta_1^\circ$	$\log \beta_2^\circ$	$\log \beta_3^\circ$	Method	Ref.	$\log \beta_1^0$
PaO(OH) ²⁺	3(Li,H,ClO ₄)	298	3.56	7.65±0.03	10.9±1.1	dis	[94]	-
							[95]	
	1 H(ClO ₄)	298	3.95	7.43	10.47	dis	[96]	-
	1(Na,H,ClO ₄)	298	5.4±0.5	10.4±1.0	15.3±1.4	qh pol	[97]	-
NpO ₂ ⁺	2 (NaClO ₄)	296	1.35			sp	[98]	-
	2 (NaClO ₄)	298	0.99±0.04			dis	[47]	-
	?	298	0.90			nmr	[48]	-
	1.0 (NaClO ₄)	294	1.2±0.1			ise	[20]	1.40
	1.0 (NaClO ₄)	296	1.26±0.12			dis	[40]	1.46
	0.1 (NaClO ₄)	294	1.5±0.2			ise	[20]	1.72
	0.1 NaClO ₄	294	1.76±0.05			ise	[20]	1.98

Table-3

Stability constants of the fluoride complexes of tetravalent actinides.



M	μ Medium	T	$\log \beta_1^0$	$\log \beta_2^0$	$\log \beta_3^0$	$\log \beta_4^0$	Method	Ref:	$\log \beta_1^0$
Tb ⁴⁺	13.0 (HNO ₃)	298	2.7	5.4	8.2	11.0	sol	[54]	-
	13.0 (HNO ₃)	323	2.8	5.8	9.1	12.6	sol	[54]	-
	13.0 (HNO ₃)	373	2.7	5.5	8.5	11.6	sol	[54]	-
	8.0 (HNO ₃)	298	3.2	5.9	8.2	10.1	sol	[54]	-
	8.0 (HNO ₃)	323	2.9	5.4	7.5	9.2	sol	[54]	-
	8.0 (HNO ₃)	373	2.9	5.5	7.9	10.1	sol	[54]	-
	4.0 (HNO ₃)	298	3.8	6.8	9.0	10.4	sol	[54]	-
	4.0 (HNO ₃)	323	3.7	6.6	8.6	9.8	sol	[54]	-
	4.0 (HNO ₃)	373	3.3	6.0	8.2	9.8	sol	[54]	-
	4.0 HClO ₄	293	4.68±0.01	7.65			ise	[11]	-
	4.0 HClO ₄	293	4.62±0.04				dis	[11]	-
	3.0 (NaClO ₄)	298	4.52±0.05	7.26±0.14	8.9±0.3		ise	[14]	-
	2.0 HClO ₄	298	4.43±0.02				dis	[60]	-
	1.0 HClO ₄	276	4.73±0.02				ise	[16]	8.51
	1.0 HClO ₄	283	4.65±0.02				dis	[16]	8.43
	1.0 HClO ₄	298	4.49±0.03				dis	[16]	8.27
	1.0 HClO ₄	298	4.51±0.02				ise	[16]	8.29
	1.0 HClO ₄	320	4.45±0.05				ise	[16]	-
	1.0 HClO ₄	328	4.33±0.02				dis	[16]	-
	1.0 (NaClO ₄)	296	$\log \beta_1$ 7.61±0.01	$\log \beta_2$ 13.42±0.05	$\log \beta_3$ 17.65±0.20	$\log \beta_4$ 23.67±0.11	ise	[22]	8.43
	0.5 (H,Na)ClO ₄	298	4.63	7.49			dis	[99]	8.67
	0.5 NaClO ₄	298	4.65±0.04	7.46±0.05	8.97±0.08		red	[9]	8.65
	0.5 NaClO ₄	298	4.70	7.46			dis	[100]	8.70
0.01 NH ₄ NO ₃	278	5.18	8.54	10.25	10.65	ise	[13]	8.51	
0.01 NH ₄ NO ₃	298	5.03	8.30	9.69	9.88	ise	[13]	8.35	
0.01 NH ₄ NO ₃	318	4.72	7.69	9.00	9.48	ise	[13]	-	
var	298	$\log \beta_1 = 5.9$	$\log \beta_2 = 8.7$			sol,sp	[53]	-	
Pa ⁴⁺	3 H(ClO ₄)	298	4.73	8.26			dis	[94] [95]-	-
U ⁴⁺	4.0 NaClO ₄	298	5.37±0.01	8.29±0.01	9.45±0.03	ise	[83]	-	
	4.0 HClO ₄	293	5.54	8.72	10.68	ise	[11]	-	
	2.0 HClO ₄	293	5.35	8.80	12.30	15.90	nmr	[101]	-
	2.0 NaClO ₄	298	.6	.8			dis	[55]	-
	1.0 NaCl	298	4.49±0.04	7.45±0.01	8.95±0.05	10.11±0.14	qh	[15]	8.27
	1.0 HClO ₄	276	4.90±0.06				ise	[16]	-
	1.0 HClO ₄	298	4.82±0.08				ise	[16]	8.60
	1.0 HClO ₄	320	4.54±0.09				ise	[16]	-
	1.0 NaClO ₄	296	$\log \beta_1$ 8.48±0.01	$\log \beta_2$ 14.66±0.01	$\log \beta_3$ 19.51±0.03	$\log \beta_4$ 23.92±0.04	ise	[22]	9.30

Table-3. (continued)

M	μ Medium	T	$\log \beta_1^*$	$\log \beta_2^*$	$\log \beta_3^*$	$\log \beta_4^*$	Method	Ref:	$\log \beta_1^0$
Np ⁴⁺	4.0 HClO ₄	293	4.82±0.02	7.57±0.08			cix	[102]	-
	4.0 HClO ₄	293	7.51±0.10	9.85±0.15	11.15		red	[102]	-
	2.0 HClO ₄	298	4.11±0.03				cix	[57]	-
	2.0 HClO ₄	298	4.70±0.06				cix	[103]	-
	2.0 HClO ₄	298	4.60±0.10	7.51			dis	[60]	-
	1.0 HClO ₄	298	4.23±0.12				cix	[57]	8.02
	1.0 HClO ₄	283	4.71±0.03				dis	[16]	-
	1.0 HClO ₄	298	4.60±0.02				dis	[16]	8.38
	1.0 HClO ₄	298	4.56±0.04				cix	[103]	8.34
	1.0 HClO ₄	303	4.52±0.02				dis	[16]	8.30
	1.0 NaClO ₄	296	$\log \beta_1$ 8.17±0.04	$\log \beta_2$ 14.52±0.13	$\log \beta_3$ 20.05±0.13	$\log \beta_4$ 25.95±0.18	ise	[22]	8.99
Pu ⁴⁺	2.0 HClO ₄	274	4.52±0.04	7.69±0.07			dis	[104]	-
	2.0 HCl	298	4.04				sp	[105]	-
	2.0 HClO ₄	280	5.50±0.03	7.54±0.03			dis	[104]	-
	2.0 HClO ₄	283	4.70±0.01	7.65±0.03			dis	[106]	-
	2.0 HClO ₄	288	4.50±0.03	7.54±0.03			dis	[104]	-
	2.0 HClO ₄	296	4.64±0.01	7.61±0.02			dis	[59]	-
	2.0 HClO ₄	298	4.45				cix	[107]	-
	2.0 HClO ₄	298	4.47±0.03	7.46±0.03			dis	[104]	-
	2.0 NaClO ₄	298	4.37±0.08	7.35±0.11			dis	[104]	-
	2.0 HNO ₃	π	3.78±0.02				cix	[58]	-
	2.0 HClO ₄	π	4.45±0.03				cix	[107]	-
	1.0 HClO ₄	298	4.20±0.09				cix	[107]	7.98
	1.0 HClO ₄	298	4.66	7.32			cou	[108]	8.44
	1.0 HNO ₃	π	4.04±0.05				cix	[58]	7.82
	1.0 HNO ₃	298	4.23				sp	[105]	8.01
1.0 NaClO ₄	296	$\log \beta_1$ 7.61±0.12	$\log \beta_2$ 14.77±0.10	$\log \beta_3$ 20.11±0.37	$\log \beta_4$ 26.07±0.16	ise	[22]	8.43	

Table-4

Stability constants of the fluoride complexes of trivalent actinides.

$$M^{3+} + nF^- = MF_n^{(3-n)+}$$

M	μ Medium	T	$\log\beta_1$	$\log\beta_2$	$\log\beta_3$	Method	Ref:	$\log\beta_1^0$
Ac ³⁺	0.5 (NaClO ₄)	298	2.72±0.01	5.22±0.02	7.90	dis	[109]	3.26
	0.1 (NaClO ₄)	298	2.95			tp	[61]	3.60
Pu ³⁺	1.0(NaClO ₄)	294	3.58±0.08	6.40±1.18	12.61±0.15	ise	[23]	4.19
Am ³⁺	1.0(NaClO ₄)	293	2.39±0.01			dis	[16]	3.00
	1.0(NaClO ₄)	298	2.49±0.02			dis	[16]	3.10
	1.0(NaClO ₄)	298	2.93±0.10			dis	[110]	3.54
	1.0(NaClO ₄)	313	2.57±0.02			dis	[16]	-
	1.0(NaClO ₄)	328	2.71±0.03			dis	[16]	-
	0.5(NaClO ₄)	298	3.39±0.01	6.11±0.02	9.00	dis	[63]	4.20
	0.1(NaClO ₄)	298	2.50±0.03	4.75±0.08		cix	[111]	3.15
	0.1(HClO ₄)	273			3.74 ^a	sol	[62]	-
	0.1(HClO ₄)	298			4.13 ^a	sol	[62]	-
	0.1(HClO ₄)	320			3.13 ^a	sol	[62]	-
	0.1(NaClO ₄)	298	3.32±0.10			tp	[61]	3.97
	0 corr	298			3.11 ^a	sol	[62]	-
Cm ³⁺	1 (NaClO ₄)	283	2.50±0.02			dis	[16]	-
	1 (NaClO ₄)	298	2.93±0.18			dis	[110]	3.54
	1 (NaClO ₄)	298	2.61±0.02			dis	[16]	3.22
	1 (NaClO ₄)	313	2.68±0.05			dis	[16]	-
	1 (NaClO ₄)	328	2.81±0.02			dis	[16]	-
	0.5(NaClO ₄)	298	3.34	6.18	9.08	dis	[63]	3.95
	0.1(HClO ₄)	273			3.87 ^a	sol	[62]	-
	0.1(HClO ₄)	296			3.90 ^a	sol	[62]	-
	0.1(HClO ₄)	320			4.37 ^a	sol	[62]	-
	0 corr (D-H)	298			4.14 ^a		[62]	-
Bk ³⁺	1 (NaClO ₄)	283	2.77±0.04			dis	[16]	-
	1 (NaClO ₄)	298	2.89±0.04			dis	[16]	3.50
	1 (NaClO ₄)	298	2.88			dis	[16]	3.49
	1 (NaClO ₄)	313	2.97±0.03			dis	[16]	-
	1 (NaClO ₄)	328	3.08±0.04			dis	[16]	-
Cf ³⁺	1 (NaClO ₄)	298	3.08±0.04			dis	[110]	3.69
	1 (NaClO ₄)	283	2.93±0.02			dis	[16]	-
	1 (NaClO ₄)	298	3.03±0.04			dis	[16]	3.64
	1 (NaClO ₄)	313	3.13±0.04			dis	[16]	-
	1 (NaClO ₄)	328	3.23±0.04			dis	[16]	-

^aValues from [62] are for $MF_2^+ + F^- = MF_3^0$

Table-5

Stability constants of fluoride complexes of actinides
at various oxidation states measured in this laboratory
using fluoride ion selective electrode.

M	μ Medium	T	$\log\beta_1$	$\log\beta_2$	$\log\beta_3$	$\log\beta_4$
H ⁺	0.01 (NaClO ₄)	298	3.09	3.60	-	-
	0.1 (NaClO ₄)	298	3.06	3.51	-	-
U(VI)	0.1 (NaClO ₄)	294	4.78 ± 0.01	8.14 ± 0.80	10.13 ± 0.17	11.66 ± 0.13
	1.0 (NaClO ₄)	294	4.56 ± 0.01	8.02 ± 0.02	10.46 ± 0.07	11.99 ± 0.25
Np(VI)	0.1 (NaClO ₄)	294	4.15 ± 0.08	7.08 ± 0.09	9.83 ± 0.07	-
	1.0 (NaClO ₄)	294	3.94 ± 0.01	6.73 ± 0.02	8.29 ± 0.01	-
Pu(VI)	0.1 (NaClO ₄)	294	4.05 ± 0.15	6.88 ± 0.15	9.06 ± 0.09	-
	1.0 (NaClO ₄)	294	3.80 ± 0.10	6.31 ± 0.12	8.00 ± 0.17	-
Np(V)	0.1 (NaClO ₄)	294	1.50 ± 0.20	-	-	-
	1.0 (NaClO ₄)	294	1.20 ± 0.10	-	-	-
Th(IV)	1.0 (NaClO ₄)	294	7.61 ± 0.01	13.42 ± 0.05	17.65 ± 0.02	23.62 ± 0.11
U(IV)	1.0 (NaClO ₄)	294	8.48 ± 0.01	14.66 ± 0.01	19.51 ± 0.03	23.92 ± 0.06
Np(IV)	1.0 (NaClO ₄)	294	8.17 ± 0.04	14.52 ± 0.13	20.05 ± 0.13	25.95 ± 0.18
Pu(IV)	1.0 (NaClO ₄)	294	7.61 ± 0.12	14.77 ± 0.10	20.11 ± 0.37	26.07 ± 0.16
Pu(III)	1.0 (NaClO ₄)	294	3.58 ± 0.08	6.40 ± 1.13	12.61 ± 0.15	-

Table-6

Metal ion parameters and stability constants of their fluoride complexes obtained from literature

Sr. No.	Metal ion	Radius (cm) (Å ⁺)	ξ_1	ξ_2	Ionic strength (M)	$\log\beta_1$	$\log\beta_1^0$
1	Ba ²⁺	1.350(6)	4	1.0	1.0	-0.15	0.26
2	Sr ²⁺	1.180(6)	4	1.0	1.0	0.15	0.56
3	Ni ²⁺	0.690(6)	8	-2.2	1.0	0.34	0.75
4	Co ²⁺	0.745(6)	8	-1.8	1.0	0.40	0.81
5	Zn ²⁺	0.600(4)	8	-3.0	0.5	0.74	1.28
6	Ca ²⁺	1.000(6)	4	1.0	1.0	0.53	0.94
7	Mn ²⁺	0.830(6)	8	-1.0	1.0	0.62	1.03
8	Cd ²⁺	0.950(6)	8	0.0	1.0	0.72	1.13
9	Fe ²⁺	0.780(6)	8	-1.4	1.0	0.83	1.24
10	Mg ²⁺	0.720(6)	8	1.0	1.0	1.32	1.73
11	Pb ²⁺	0.980(4)	8	1.0	1.0	1.46	1.87
12	La ³⁺	1.160(8)	4	2.0	0.5	2.68	3.49
13	Ac ³⁺	1.120(6)	8	2.0	0.5	2.69	3.50
14	Pr ³⁺	1.126(8)	10	2.0	1.0	3.01	3.62
15	Nd ³⁺	1.109(8)	10	2.0	1.0	3.09	3.70
16	Sm ³⁺	1.079(8)	10	2.0	1.0	3.12	3.73
17	Ce ³⁺	1.143(8)	10	2.0	0.5	3.12	3.93
18	Eu ³⁺	1.066(8)	10	2.0	1.0	3.19	3.80
19	Gd ³⁺	1.053(8)	10	2.0	1.0	3.36	3.97
20	Er ³⁺	1.004(8)	10	2.0	1.0	3.54	4.15
21	Yb ³⁺	0.985(8)	10	2.0	1.0	3.58	4.19
22	Lu ³⁺	0.977(8)	10	2.0	1.0	3.61	4.22
23	In ³⁺	0.800(6)	10	1.0	1.0	3.75	4.36
24	Y ³⁺	0.900(6)	10	2.0	0.5	3.91	4.72
25	Ga ³⁺	0.620(6)	10	-2.0	1.0	4.40	5.01
26	Fe ³⁺	0.645(6)	10	0.0	1.0	5.15	5.76
27	Mn ³⁺	0.645(6)	10	0.4	2.0	5.64	5.60
28	Sb ³⁺	0.760(6)	10	2.0	2.0	6.13	6.09
29	Sc ³⁺	0.745(6)	10	2.0	0.5	6.22	7.03
30	Ce ⁴⁺	0.870(6)	12	3.0	1.0	7.57	8.39
31	Zr ⁴⁺	0.840(8)	12	3.0	1.0	8.27	9.09

Table-7

Comparison of different models tried for linear correlation of the formation constants of the fluoride complexes of metal ions.

Y-axis : Thermodynamic formation constants β_1^0
X-axis : Function of metal ion and ligand parameters.

Model No.	Based On	X-axis	Slope	Intercept	Corr. Coeff.
1.	Charge Density of metal ions	$\frac{Z_+}{r_+^2}$	0.768 ± 0.198	0.740 ± 0.799	0.5850
2.	Ionic Potential of metal ions	$\frac{Z_+}{r_+}$	2.083 ± 0.259	-2.861 ± 0.831	0.8308
3.	Born equation for ion-dipole interaction	$\frac{Z_+^2}{r_+}$	0.530 ± 0.032	-1.062 ± 0.309	0.9505
4.	Effective ionic radius of the Hydrated cation	$\frac{Z_+^2}{r_+ + 0.85}$	1.253 ± 0.058	-1.535 ± 0.258	0.9698
5.	Coloumbic attraction between +ve and -ve ions	$\frac{Z_+}{r_+ + r_-}$	7.965 ± 0.380	-6.111 ± 0.472	0.9686
6.	BSE equation taking into account both metal ion and ligand properties.	$g_1 \left[\frac{Z_+}{r_+^2} + g_2 \right]$	0.089 ± 0.002	-0.319 ± 0.101	0.9928

Z_+ : Number of +ve charges on the metal ion.

r_+ : Ionic radius of the metal ion (Shannon 1976).

r_c : Crystal radius (ionic radius + 0.14) of the metal ion.

r_- : Radius of the anion (1.33 Å for F⁻).

g_1 & g_2 : Parameters of BSE equation (see text).

Table-8

Comparison of Experimental and Calculated β_1^0 Values of
Tetravalent and Trivalent Actinides Using Different Models.

Metal ion	Electronic Config.	Ionic Radius (Cord.No.)	ξ_1	ξ_2	Experimental β_1^0	Calculated β_1^0			
						Born Eqn. Model-3	Born Eqn(r_{ion}) Model-4	Columbic Attraction Model-5	BSE Eqn. Model-6
Th ⁴⁺	5f ⁰ 6d ⁰	0.94(6)	12	3	8.43	7.96	8.86	7.92	7.69
Pa ⁴⁺	5f ⁰ 6d ¹	0.90(6)	12	3.5	*	8.37	9.08	8.18	8.69
U ⁴⁺	5f ⁰ 6d ²	0.89(6)	12	3.9	9.30	8.47	9.13	8.24	9.21
Np ⁴⁺	5f ² 6d ¹	0.87(6)	12	3.5	8.99	8.69	9.25	8.37	8.98
Pu ⁴⁺	5f ⁴ 6d ⁰	0.86(6)	12	3.0	8.43	8.80	9.31	8.44	8.63
Pu ³⁺	5f ⁵ 6d ⁰	1.00(6)	10	2.0	4.19	3.71	4.13	4.14	4.12
Am ³⁺	5f ⁶ 6d ⁰	0.975(6)	10	2.0	4.20 ^{**}	3.83	4.21	4.26	4.25

* No reliable value

** From Ref. [63]

** Though this value ($\log \beta_1^0 = 4.20$) is in agreement with the calculated values it appears to be doubtful. Choppin et al [16] and Nash et al [111] obtained $\log \beta_1^0$ values around 3.15. The value $\log \beta_1^0$ obtained in our recent work is 3.09 [23a]

Table-9

Calculation of $g_1(Z_+ / r_+^2 + g_2)$ for the complexes of the oxoactinide cations with some ligands of known pK

Oxo-cation	Ligand	$\log\beta_1(\mu)$	Ref.	$\log\beta_1^0$	Int.	Slp	F**	pK _a
UO ₂ ²⁺	OH ⁻	-4.77 [†] (1.0)	[112]	9.64	-0.52	0.139	73.1	14.00
	CO ₃ ²⁻	8.3(0.5)	[113]	9.38	2.13	0.104	69.7	10.33
	CH ₃ COO ⁻	3.0(0.1)	[81]	3.43	-0.13	0.066	53.9	4.86
	SO ₄ ²⁻	3.36(0)	[64]	3.36	1.10	0.050	45.2	1.99
	IO ₃ ⁻	1.58(0.1)	[114]	2.01	0.03	0.042	47.1	0.51
NpO ₂ ²⁺	OH ⁻	-5.17 [†] (1.0)	[115]	9.03	-0.52	0.139	68.7	14.00
	CH ₃ COO ⁻	2.98(0)	[81]	2.98	-0.13	0.066	47.1	4.86
	SO ₄ ²⁻	3.40(0)	[64]	3.40	1.10	0.050	46.0	1.99
	IO ₃ ⁻	0.61(0.3)	[116]	1.15	0.03	0.042	26.7	0.51
	H ₂ PO ₄ ⁻	2.33(0)	[117]	2.33	0.17	0.049	44.1	2.16
PuO ₂ ²⁺	OH ⁻	-5.97 [†] (1.0)	[118]	8.23	-0.52	0.139	64.5	14.00
	CH ₃ COO ⁻	2.13(1.0)	[81]	2.54	-0.13	0.066	40.4	4.86
	SO ₄ ²⁻	2.23(2.0)	[41]	2.20	1.10	0.050	22.0	1.99
	H ₂ PO ₄ ⁻	2.30(0)	[117]	2.30	0.17	0.049	43.5	2.16
NpO ₂ ⁺	OH ⁻	-10.08 [†] (1.0)	[119]	3.92	-0.52	0.139	31.9	14.00
	IO ₃ ⁻	0.58(2.0)	[98]	0.50	0.03	0.042	12.9	0.51
	H ₂ PO ₄ ⁻	0.81(0.2)	[120]	1.32	0.17	0.049	23.5	2.16
	CO ₃ ²⁻	4.90(0)	[121]	4.90	2.13	0.104	26.6	10.33
	HPO ₄ ²⁻	3.40(0)	[120]	3.40	0.80	0.106	24.5	7.05

* Hydrolysis reaction

** F = $g_1(Z_+ / r_+^2 + g_2)$

Table-10

Calculated and experimental values of β_1^0 of the fluoride complexes
of oxometal actinides using BSE equation.

Oxo- cation	Int.	Slp	R [*]	F	β_1^{0**} (calc.)	β_1^0 (exptl.)
UO ₂ ²⁺	43.74 ± 2.11	2.218 ± 0.260	0.9800	60.24	5.04	4.97
NpO ₂ ²⁺	34.67 ± 4.30	2.520 ± 0.636	0.9162	53.42	4.43	4.37
PuO ₂ ²⁺	27.80 ± 8.14	2.463 ± 1.078	0.8504	46.12	3.78	4.21
NpO ₂ ⁺	16.37 ± 2.76	1.102 ± 0.327	0.8894	24.57	1.87	1.72

** pK_a^0 of hydrofluoric acid was taken as 7.44 as obtained
from equation 18.

* R = Regression Coefficient: $F = g_1(Z_+ / r_+^2) + g_2$

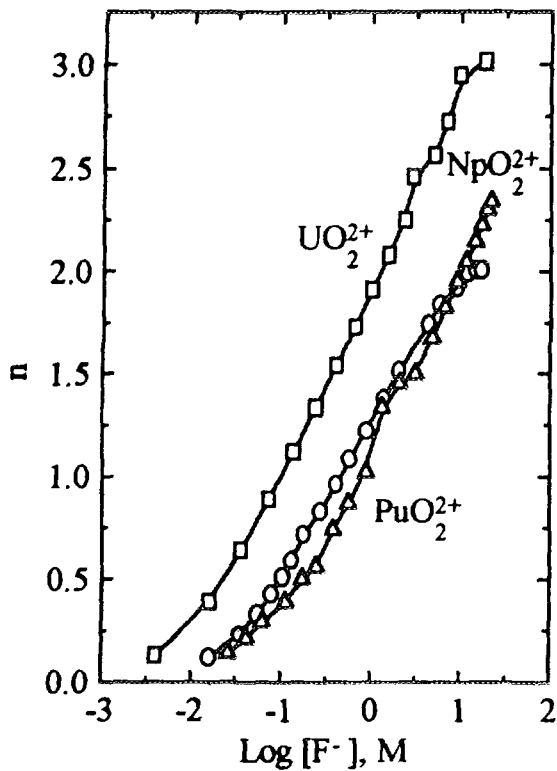


Fig. 1 : Formation function of the fluoride complexes of hexavalent actinides.

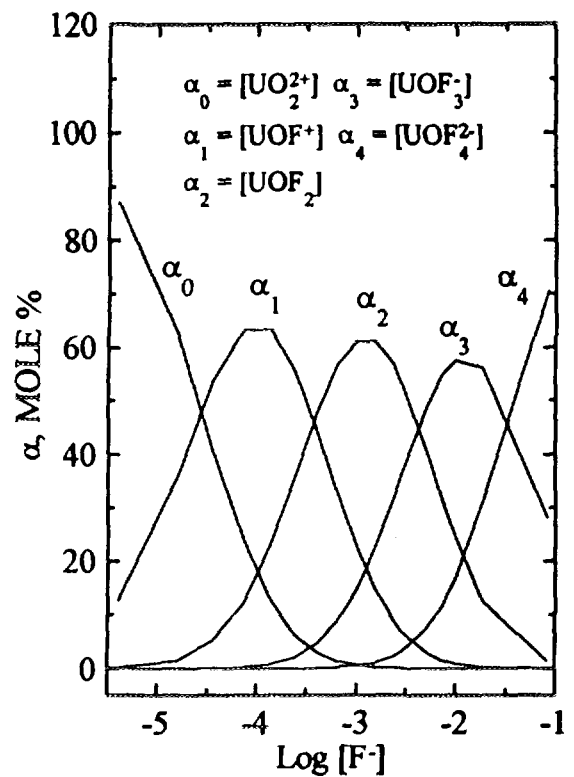


Fig 2 : Distribution of UO_2^{2+} among the different complexes at varying $[F^-]$

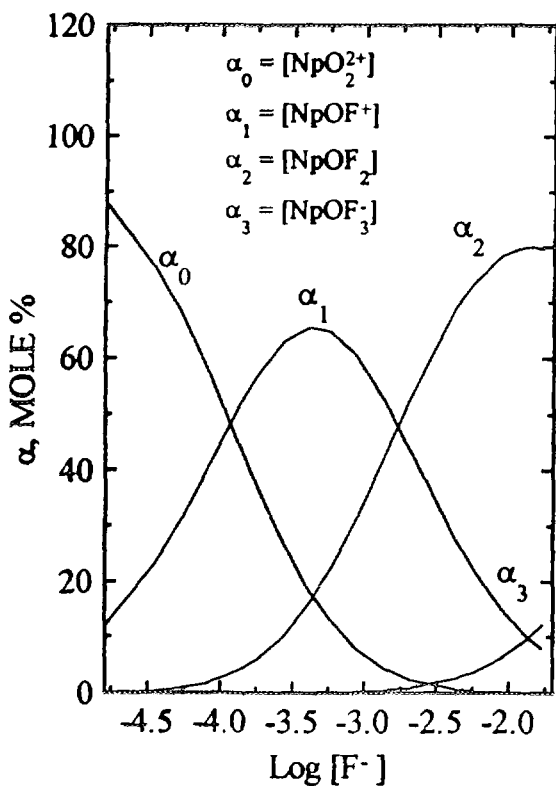


Fig 3 : Distribution of NpO_2^{2+} among the different complexes at varying $[F^-]$

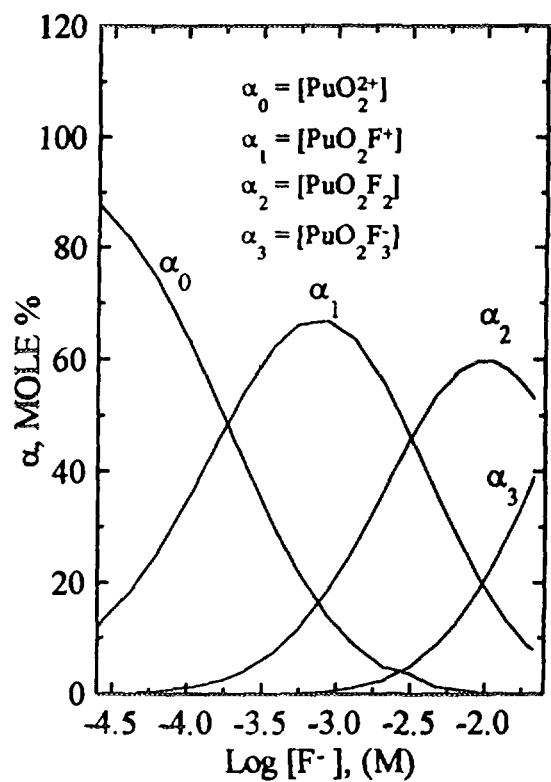


Fig 4 : Distribution of PuO_2^{2+} among the different complexes at varying $[F^-]$

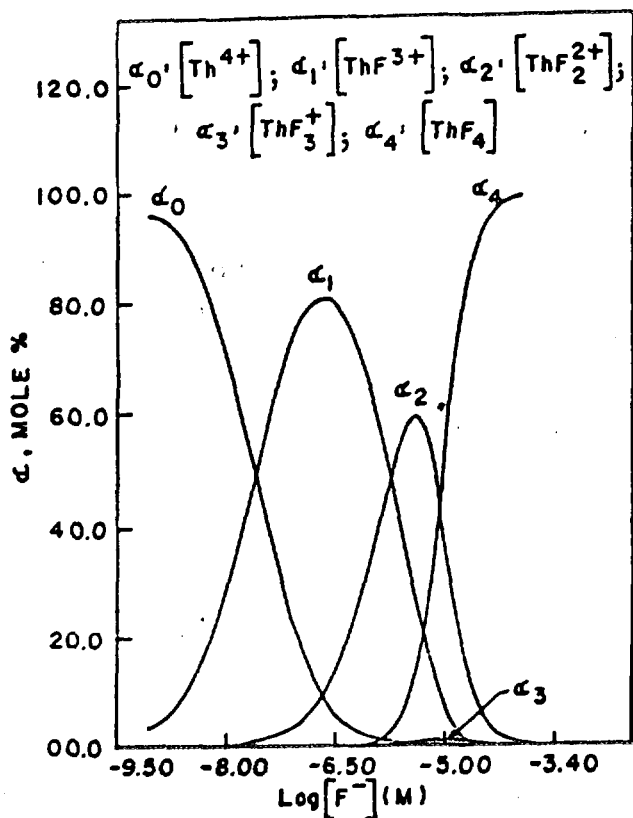


FIG.-5. THE DISTRIBUTION OF THORIUM(IV) BETWEEN THE DIFFERENT COMPLEXES AT VARYING $[F^-]$.

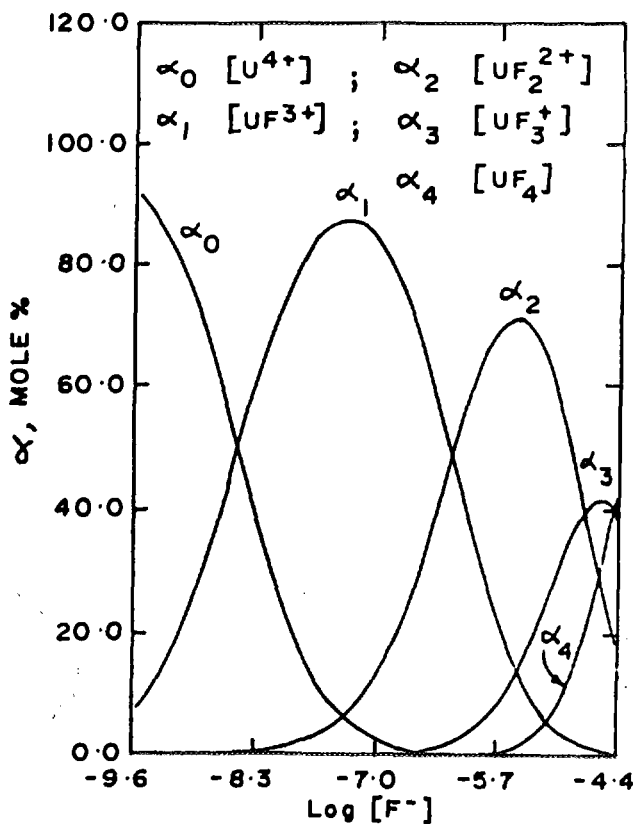


FIG.-6. THE DISTRIBUTION OF URANIUM(IV) BETWEEN THE DIFFERENT COMPLEXES AT VARYING $[F^-]$.

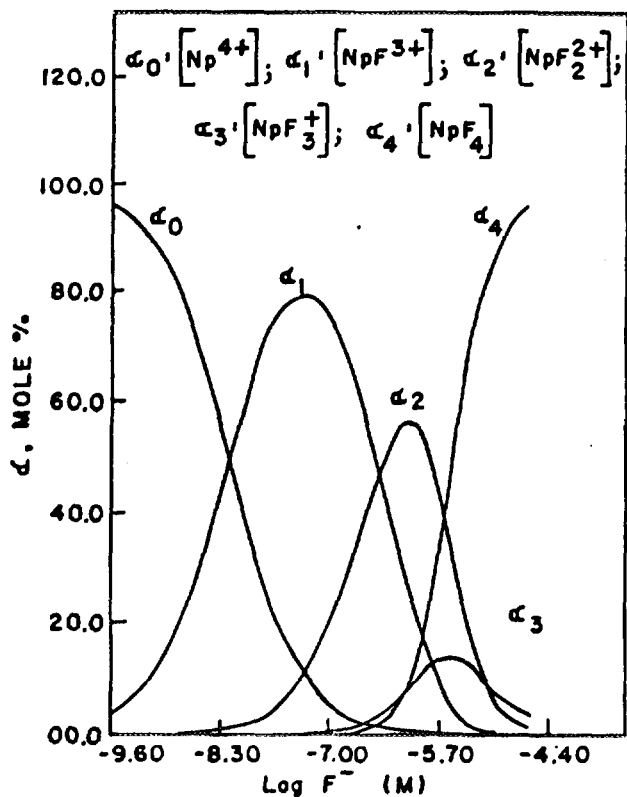


FIG.-7. THE DISTRIBUTION OF NEPTUNIUM(IV) BETWEEN THE DIFFERENT COMPLEXES AT VARYING $[F^-]$.

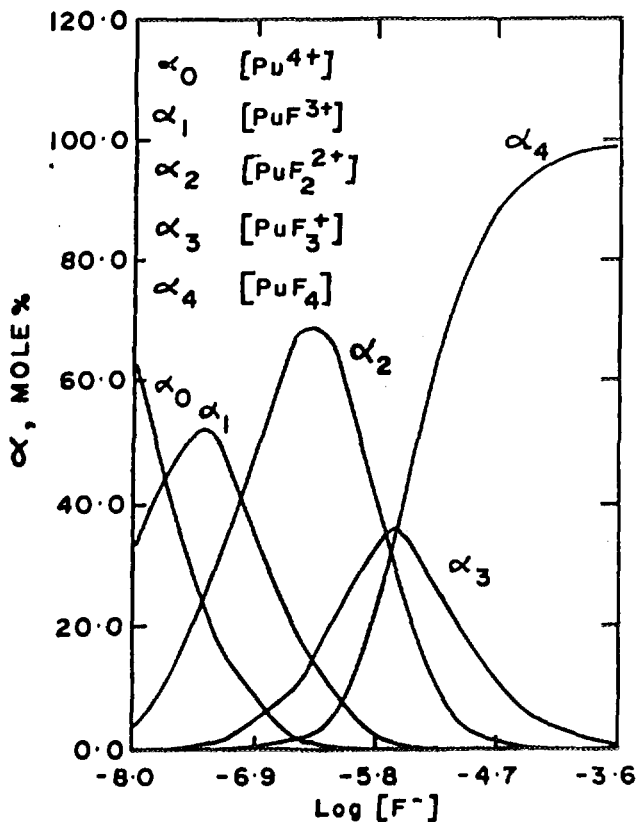


FIG.8 . THE DISTRIBUTION OF PLUTONIUM(IV) BETWEEN THE DIFFERENT COMPLEXES AT VARYING $[F^-]$.

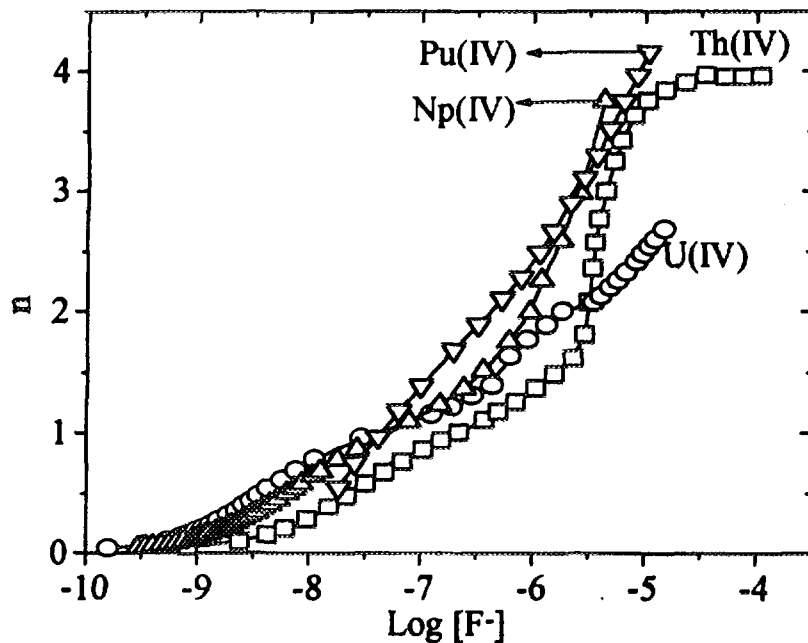


Fig. 9: Complex formation function for Th(IV)-, U(IV)-, Np(IV)- and Pu(IV)-Fluoride systems.

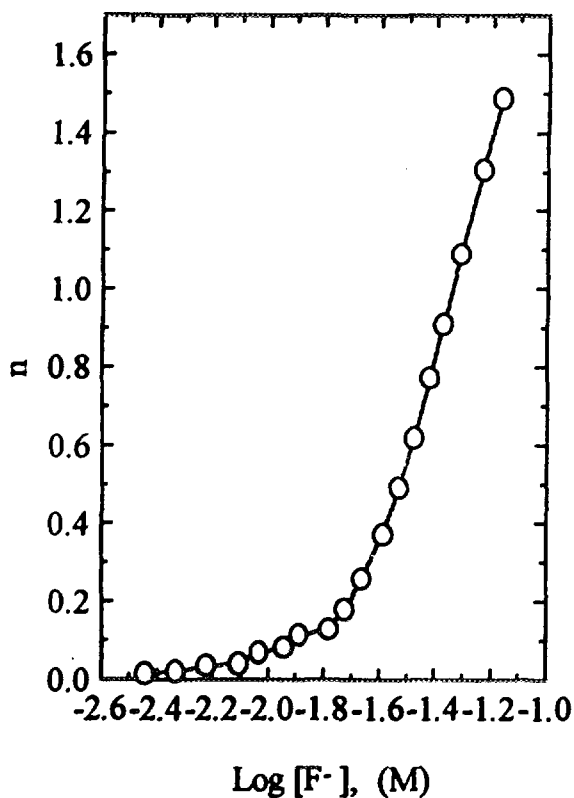


Fig 10 : Formation function of the fluoride complexes of Pu(III).

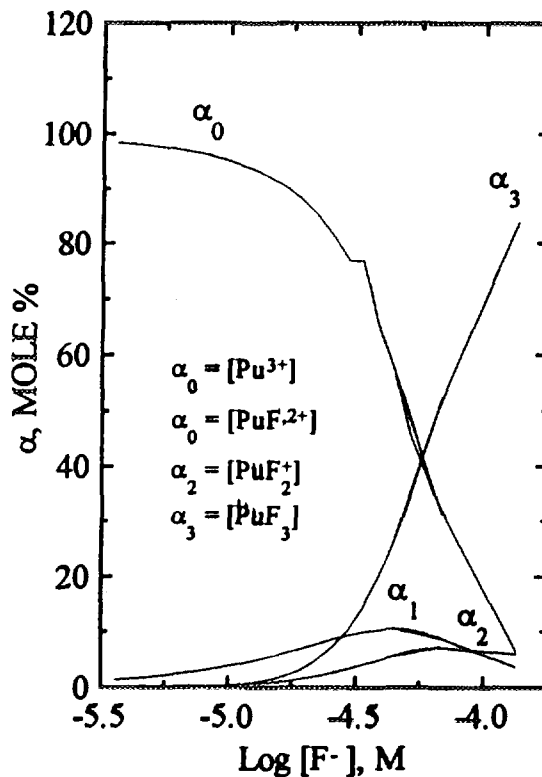


Fig 11: Distribution of Pu ³⁺ among the different complexes at varying [F⁻]

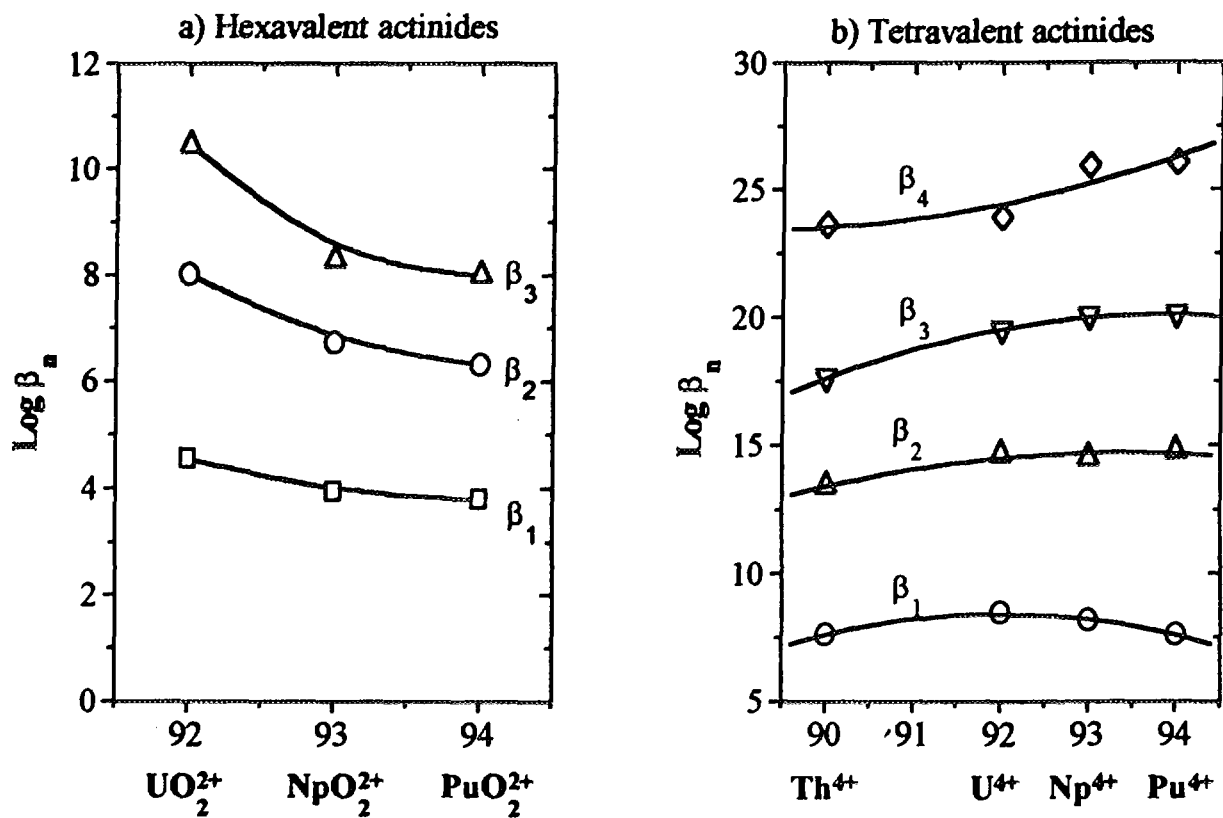


Fig. 11A: Variation of $\log \beta_n$ of the fluoride complexes with increasing atomic number of the actinide in hexavalent and tetravalent states.

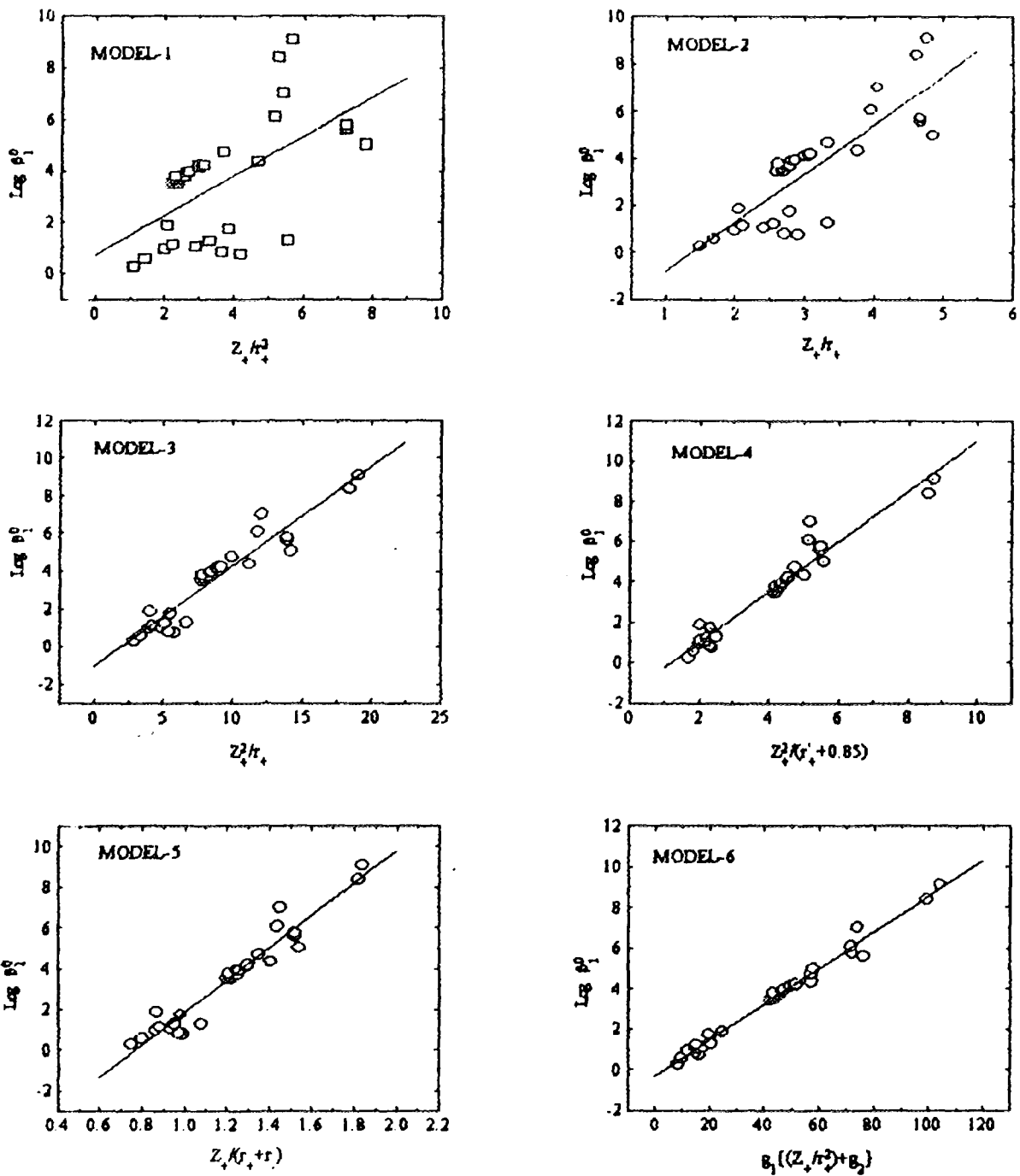


Fig 12: Linear correlation of the stability constants of the fluoride complexes with various functions of metal ion and ligand parameters as given in Table-7.

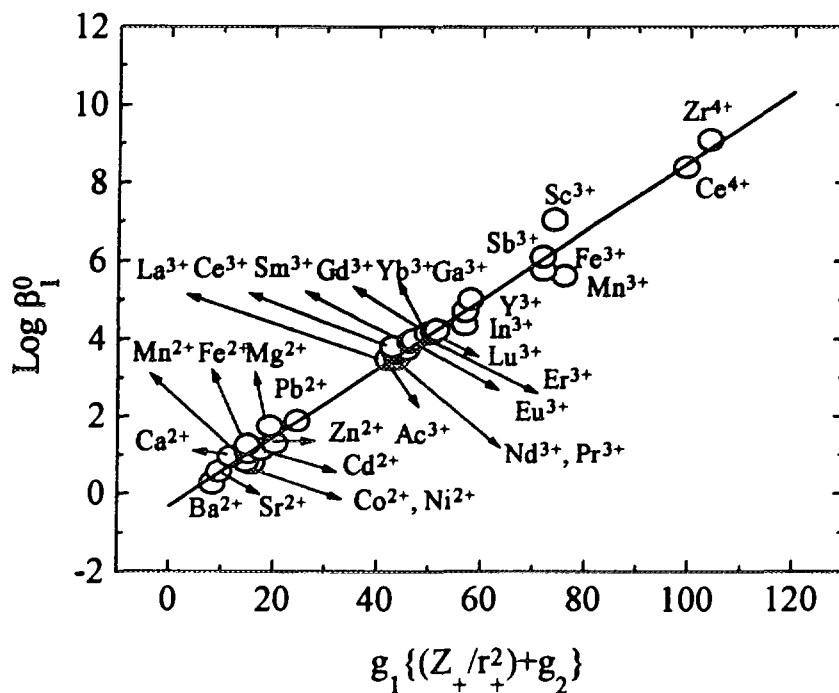


Fig. 13: Linear correlation of the stability constants of the fluoride complexes metal ion the BSE parameters (45) involving charge, radius and electronic structure of the metal ion.

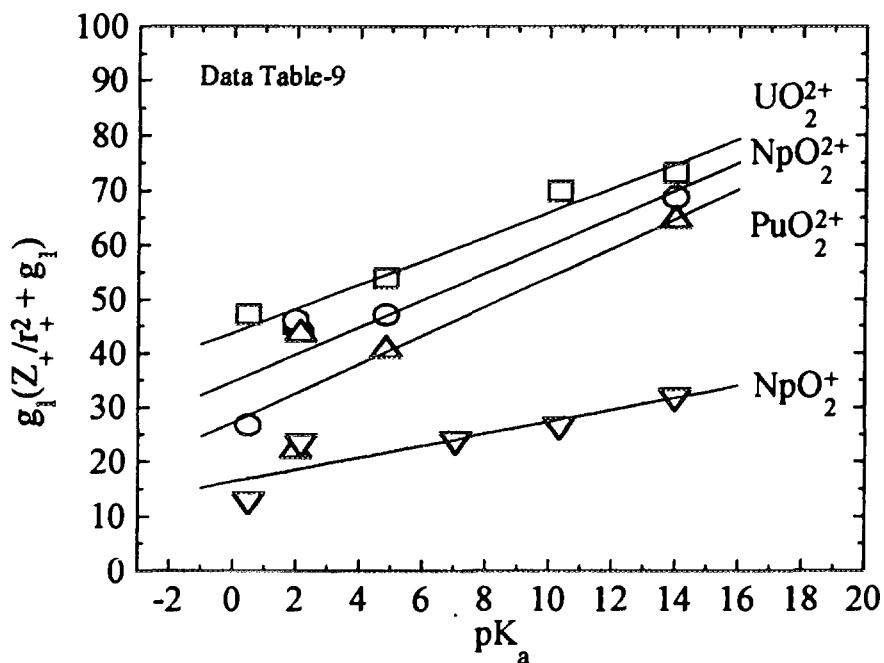


Fig 14 : Plot of BSE functions calculated from literature β_1^0 values vs pK_a of the ligand.

