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RADIOCHEMICAL STUDIES OF SOME TRANSPLUTONIUM ELEMENTS

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Abstract - Radiochemical studies undertaken by the groups of radioelectrochemistry and gas thermochromatography of the laboratory of radiochemistry are reviewed. Radiocoulometric and radiopolarographic methods suitable for studies of elements at the tracer scale concentration level are briefly described. These two techniques have been recently used for studying the chemistry of mendelevium in aqueous solution. It was concluded that mendelevium is reduced at - 1.50 V/NHE in non complexing medium ; effect of citrate, acetate and chloride ions indicates that its chemistry is very similar to this of divalent fermium. It cannot be considered as a cesium like or silver like ion in the experimental conditions. Preliminary experiments are described on diffusion coefficient measurements of some lanthanide and actinide ions in aqueous solution. Trivalent americium and europium ions have similar Stokes radii, as expected, but first experiments on californium and einsteinium seem to indicate differences with lanthanide homologues.

The gas thermochromatographic method has been applied to the study of the tetravalent fluorides of Pu, Am, Cm, Bk, Cf and Es. Deposition temperature T_c has been measured for all the considered elements. They are compared to this of penta and hexafluorides. The value obtained for einsteinium, T_c = 695° C is consistent with the existence of the gaseous EsF_4 compound. This is the first experimental indication of the existence of tetravalent einsteinium, which would be thermaly less stable than that of the lighter actinides.

Finally some thermodynamical consequences of these data are drawn. 3/0 redox potentials are estimated and stability of oxidation states (2 to 6) are compared in the actinide series. Enthalpy of hydration is also calculated with a semi empirical expression.

INTRODUCTION

In this report, I present an overview of recent radiochemical studies of heavy actinides, undertaken by the radiochemistry groups of the Institut de Physique Nucléaire.

It is well known that many of the chemical and thermodynamical data are lacking for the second half of the actinide series. Therefore one must develop radiochemical methods applicable to the tracer scale amount of studied element and even applicable to the level of hundreds of atoms.

Electrochemical data obtained by radioelectrochemistry as well as data on fluoride compounds of some actinides obtained by gas thermochromatography will be presented. Moreover, I will describe new experiments we have just started for transport parameter measurement of ions in aqueous solutions. These experiments will able us to get information on the charge, radius and structure of the hydrated ions. Preliminary results on the diffusion coefficient determination of some 4 f and 5 f ions are also reported. Finally, I will draw some thermodynamical consequences of these studies.

RADIOELECTROCHEMISTRY

Radioelectrochemical investigations mainly on the heaviest actinide elements are of special interest. Further to their big advantage of being applicable to the tracer scale amount, they allow good reliability and comparable accuracy to that of classical electrochemistry. However the limitation of these methods is that only reduction of actinide ions to the metallic state with amalgam formation can be investigated. The oxidation of an actinide amalgam may also be considered. The distribution of the actinide in the two phases i.e. mercury as a working electrode and the bulk solution, is easily followed by radioactivity measurements.

We considered two cases :

. With a large cathodic area A, the concentration C of the element in the bulk of solution depends on time of electrolysis : we have the "radiocoulometric" method (1).

. On the other hand, when the area A is small, for example in case of a dropping mercury electrode (D.M.E.), C is essentially constant : we have polarographic conditions. In such case, one can obtain radiopolarogram by plotting the number of amalgamated atoms with the applied potential similarly as in the D.C. polarography.

One can also applies "pulse radiopolarography" in order to measure kinetic parameters (2).

One can therefore define the number n of exchanged electrons, half-wave potentials and kinetic parameters α and k_e^o for irreversible process.

Radiocoulometry

Controlled potential electrolysis at a mercury pool were investigated with a three electrode cell on solutions of actinides at tracer scale concentration.

At the difference of coulometry where the number of Faraday which goes through the cell is measured (dc/dt vs time curves), one can here measure the specific radioactivity of the electrolyte vs time : C = f(t).

The theoretical function C = f(t) has been obtained in a recent work (1) taking into account Fick law, cathodic potential E, electrochemical parameter, kinetics of a chemical reaction preceding the electroreduction and different experimental parameters such as volume V, diffusion layer thickness δ , cathodic area A.

The expression for a pure electrochemical reaction is given in eq. I

$$\text{I} \qquad \frac{C}{C^\circ} = \frac{1}{1+\frac{V_1}{V_2}\exp\left[\frac{nf}{RT}(E-E^\circ)\right]} \exp\left\{-\frac{S}{V_1}\,\frac{D_2}{\delta_2}\left[\frac{1+\frac{V_1}{V_2}\exp\frac{nF}{RT}(E-E^\circ)}{\frac{D_2\delta_1}{\delta_2 D_1}+\exp\frac{nF}{RT}(E-E^\circ)+\frac{D_2}{\delta_2 k_e^\circ}\exp\frac{\alpha nF}{RT}(E-E^\circ)}\right]\right\}t + \frac{1}{1+\frac{V_2}{V_1}\exp\left[-\frac{nF}{RT}(E-E^\circ)\right]}$$

Experimentally we proposed to measure the initial slope of the C = f(t) curve which can generally be obtained as the time τ of half reaction. The expression of τ is written in eq. II. One notices that τ is an experimental parameter which can be measured even with tracer-scale concentration.

$$\text{II} \qquad \tau = 0{,}693\,\frac{V_1}{S}\,\frac{\delta_2}{D_2}\left\{\frac{D_2\delta_1}{\delta_2 D_1} + \exp\left[\frac{nF}{RT}(E-E^\circ)\right] + \frac{D_2}{\delta_2 k_e^\circ}\exp\left[\frac{\alpha nF}{RT}(E-E^\circ)\right]\right\}$$

One derives a more general equation for C and τ , by considering the case of a preceding chemical reaction, when actinide ions are complexed for example with citrate ions, to prevent hydrolysis.

In that case one has to consider the kinetics of the forward (k_f) and backward chemical reaction (k_b) and of constant of formation β of the complex. The new relation of C is :

$$\text{III} \qquad C/C^\circ = 1/2G\left[(G + L - p)\exp(-L + G)t + (G - L + p)\exp(-L - G)t\right]$$

with

$$L = 0.5\,(k_f + k_b + p) \qquad G = (L^2 - k_f p)^{1/2} \qquad p = -\left[d(\log C/C^\circ)/dt\right]_{t=0}$$

An important result is that by differentiation one get the same expression (II), as previously, for t = 0.

As example theoretical and experimental curves log τ = f(E) are given on fig. 1. It concernes data obtained with Am, Cm, Bk, Cf, Es and Fm in 0.1 M Li_3Cit at 5° C. The experimental curves are similar to these calculated from the theoretical expression. One see that in the observed conditions, the electrochemical reaction proceeds irreversibly.

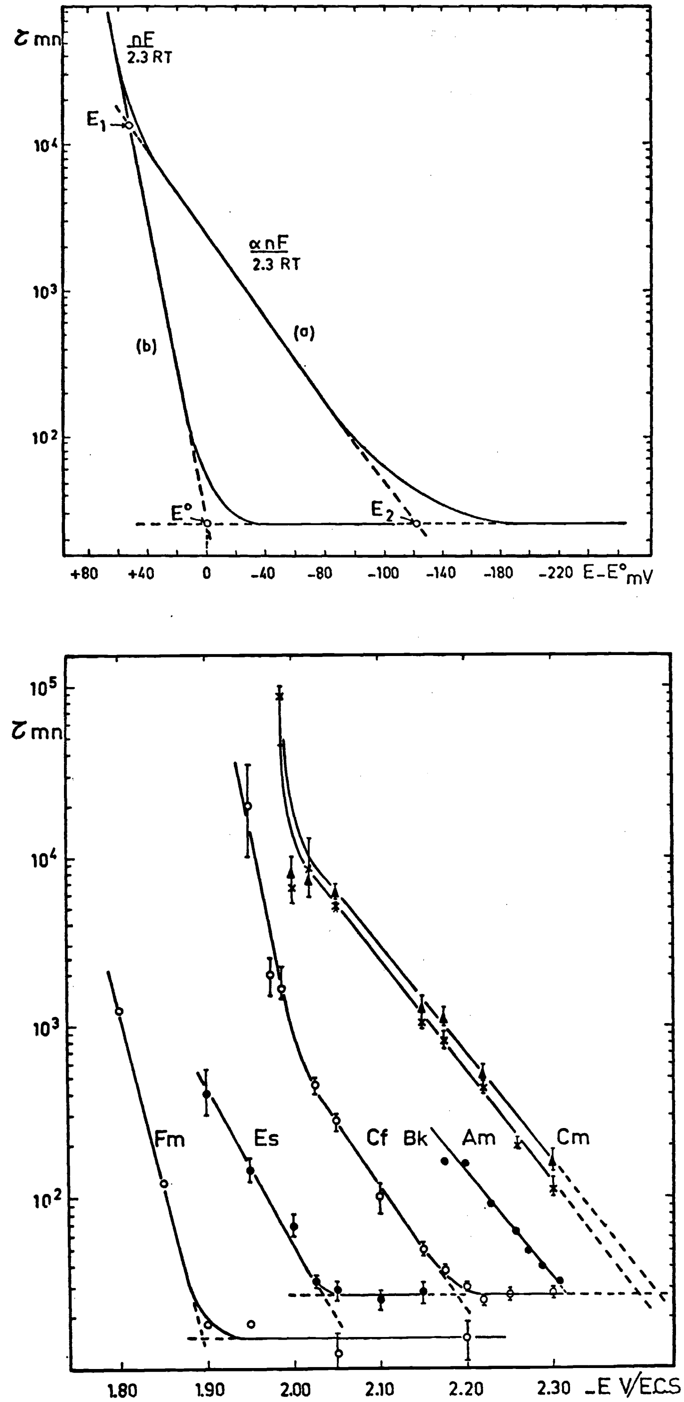

Fig. 1. Theoretical (above) and experimental curves (below) log τ = f(E) for Am , Cm, Bk, Cf, Es and Fm. 0.1 M Li_3Cit, T = 5° C. Solution volume is 4 mℓ and mercury volume is 2 mℓ . Cathode area is 4 cm^2.

Another convenient way to exploit the experimental data is to plot the ratio τ_d/τ vs E, where τ_d is the limiting value of τ observed at the most negative potentials. τ can be related to the intensity i^o at the beginning of the experiments. One shows that :

$$\tau_d/\tau = i^o/i^o_d$$

Therefore the variation of the ratio vs E is similar to a polarographic wave. We used such graph to compare electrochemical properties of mendelevium with fermium and other actinides.

Recent radiocoulometric experiments on mendelevium have been performed at the Oak Ridge National Laboratory with the collaboration of R. L. Hahn and coworkers (3). Mendelevium for these experiments was prepared via the reaction ^{254}Es(α, 2n)^{256}Md using alpha particles from the Oak Ridge Isochronous Cyclotron (ORIC). Each I-hour irradiation produced 2 x 10^4 atoms of ^{256}Md. Radiocoulometry microcell accomodating 200 $\mu\ell$ of solution and 200 $\mu\ell$ of mercury was used.

The chemistry of mendelevium is particularly interesting since Mikheev and coworkers claimed in 1973 the stability of a monovalent state of Md in alcoholic-aqueous solution (4). According to this, Md would be the unique element of both landhanide and actinide series obtainable in a + 1 oxidation state in solutions. The expected f^{14} electronic configuration of an eventual Md^+ leads to an interesting question about a cesium - like or silver - like monovalent ions, knowing that Ag^+ (d^{10}) and Md^+ (f^{14}) have both complete electronic subshell.

For that purpose we used the fact that the waves are shifted to negative potentials when the ions are complexed with ligands. For example we verified that citrate ions (0.1 M) which make strong complexes with trivalent actinides and lanthanides (log $\beta \sim 12$) shift the wave of more than 200 mV, waves of divalent barium (log $\beta \sim 3$) (5), europium or fermium (6) ions are shifted in the same conditions of $\sim$ 90 mV and waves of alkalis are not significantly affected by the presence of citrate ions according to the fact that these ions do not form complexes with citrate ions.

In case of acetate ligand the corresponding complexes are much weaker and with 0.1 M one observes a shift ΔE = 20 mV for M^{3+} ions and $\Delta E \sim 0$ for M^+ or M^{2+} ions.

Radiocoulometric experiments have been performed with 0.1 M ammonium acetate (pH 4.7) and 0.1 M ammonium citrate (pH $\sim$ 6) solutions at room temperature. Am, Cf, Es, Fm and Md isotopes have been simultaneously studied. Half time of amalgamation τ has been measured at different cathodic potential. The plots of τ_d/τ vs E are shown for Fm and Md elements in citrate and acetate medium (fig. 2). We see that Fm and Md present very close

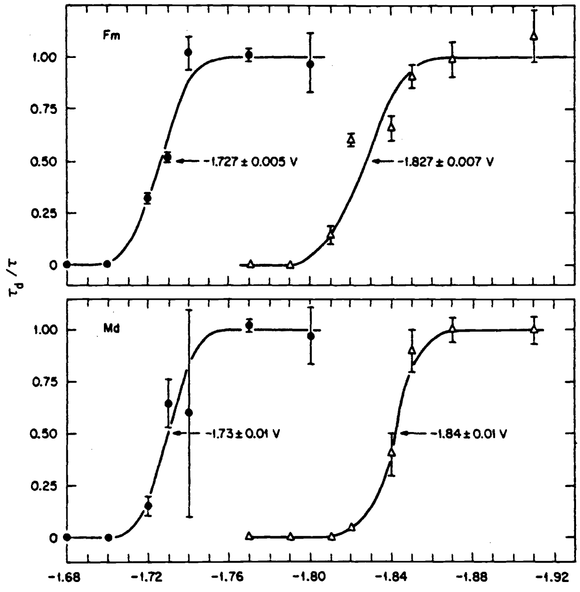

Fig. 2. Equivalent current-potential curves of ^{255}Fm and ^{256}Md obtained in 0.1 M ammonium acetate buffer (left, ●) and 0.1 M ammonium citrate at pH $\sim$ 6 (right, Δ).

properties. The shift between acetate and citrate is for both elements around 90-100 mV. It is exactly the one measured for a divalent element like barium (5) or europium.

The experimental fact one observes a significant shift with mendelevium in citrate medium means that this element cannot be considered in the experimental conditions as a cesium like ions.

The other possibility to examine is the existence of a monovalent Md^+ ion similar to Ag^+ or Cu^+. If one expect such similarity strong complexation of Md^+ with citrate or Cl^- ions could be observed and therefore the similar shift observed with Fm and Md should be fortuitus and not significant.

This is the reason why we undertook experiments by radiopolarography at Berkeley in collaboration with K. Hulet and coworkers (Lawrence Livermore Laboratory)(7).

Radiopolarography

As previously indicated this method is transposed from polarography. Radioactivity replaced the measurement of diffusion intensity. Determination of half wave potential and slope of the logarithmic transformed waves, accuracy, verification of the Ilkovic equation is similar in both methods.

Diffusion controlled radiopolarographic waves i.e. A = f(E) curves have been obtained for Am^{3+} Cm^{3+}, Cf^{3+} (8), Bk^{3+}, Es^{3+} and Fm^{3+} ions (6) in aqueous solutions at pH less than 2.7. At higher pH perturbed waves were obtained because of hydrolysis effect of actinide ions in the diffusion layer where pH is supposed to be higher than pH in the bulk solution. The analysis of the radiopolarograms showed that Am^{3+}, Cm^{3+}, Cf^{3+}, and Es^{3+} undergo a direct reduction step to the metallic state. Whereas on the other hand we obtained the first experimental indication on the existence of Fm^{2+} in aqueous solution whereas Mikheev et al. have stated in earlier work (9) the existence of Fm^{2+} in alcooholic media. The radiopolarogram of ^{255}Fm (fig. 3) corresponds to the $Fm^{2+} \longrightarrow Fm^0$ reduction process. This result was confirmed by examining the shift of the measured half wave potential by the effect of complexing (citrate) ions.

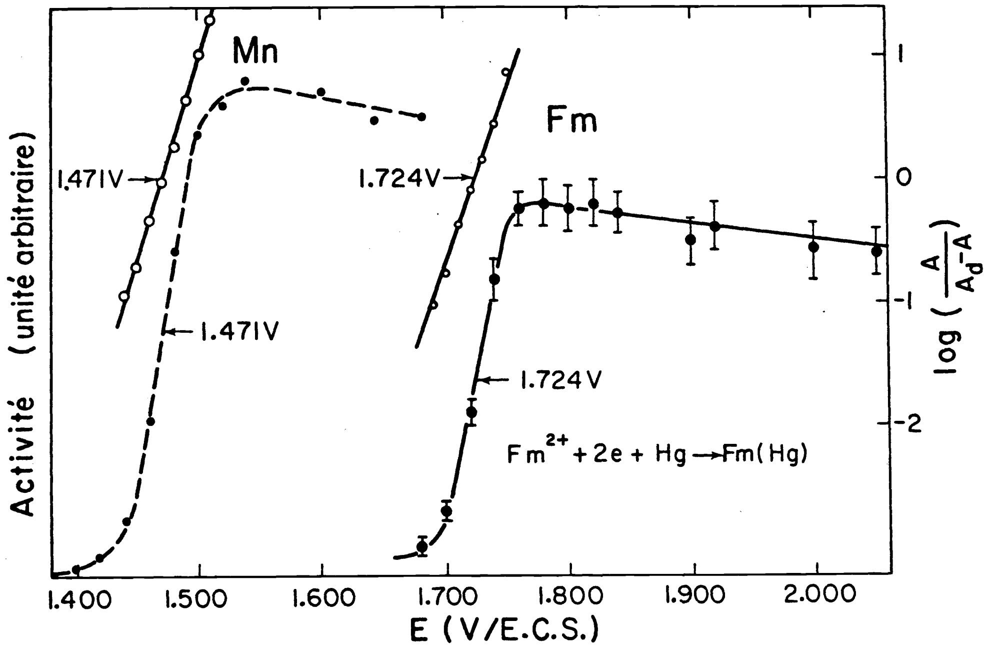

Fig. 3. Radiopolarogram of ^{255}Fm and ^{54}Mn with logarithmic transformed. 0.1 M LiCl, pH = 2.4, T = 25° C. Error bars correspond to statistical errors of ^{255}Fm radioactivity. ^{54}Mn polarogram is used as reference.

The mendelevium used for radiopolarographic experiments was prepared by irradiating a 0.7 g ^{254}Es target with the α beam of 88" cyclotron of the Lawrence Berkeley Laboratory. Each two-hr irradiation produced about 10^6 atoms of ^{256}Md and ^{257}Md. The determination of Md consisted of measuring the total spontaneous fissions produced from the daughter ^{256}Fm decay. Md was also measured from the 10 % alpha-particle branching decay of ^{256}Md and ^{257}Md.

Radiopolarograms of Cf, Es, Fm and Md were obtained simultaneously using a three electrode microcell which accomodates 100 to 200μℓ of solution. Half wave potentials have been measured in tetramethylammonium perchlorate as supporting electrolyte at pH 2.4. The data corroborate these obtained previously with Cf, Es and Fm. In case of mendelevium, the obtained half wave potential is in agreement with the one measured with acetic medium at Oak Ridge. In chloride media the results did not show any significant change in the measured values. We concluded then that chloride ions do not provide a shift due to a silver like complexed mendelevium monovalent ion. Futhermore the logarithmic transformed of the wave (Fig. 4) seems to exhibit a much different slope value than that one can expect for a 1-electron exchange electrode process (dashed line) all these evidences support the existence of divalent mendelevium ion in the experimental conditions. Consequently the value of half wave potential obtained at -1.50 V vs NHE was attributed to the $M^{2+} \rightarrow Md(Hg)$ electrode reaction. The slope of 30 mV of the logarithmic transformed wave as well as the similar behavior of Md to Fm^{2+} with regard to the complexation and reduction are consistent with our conclusion.

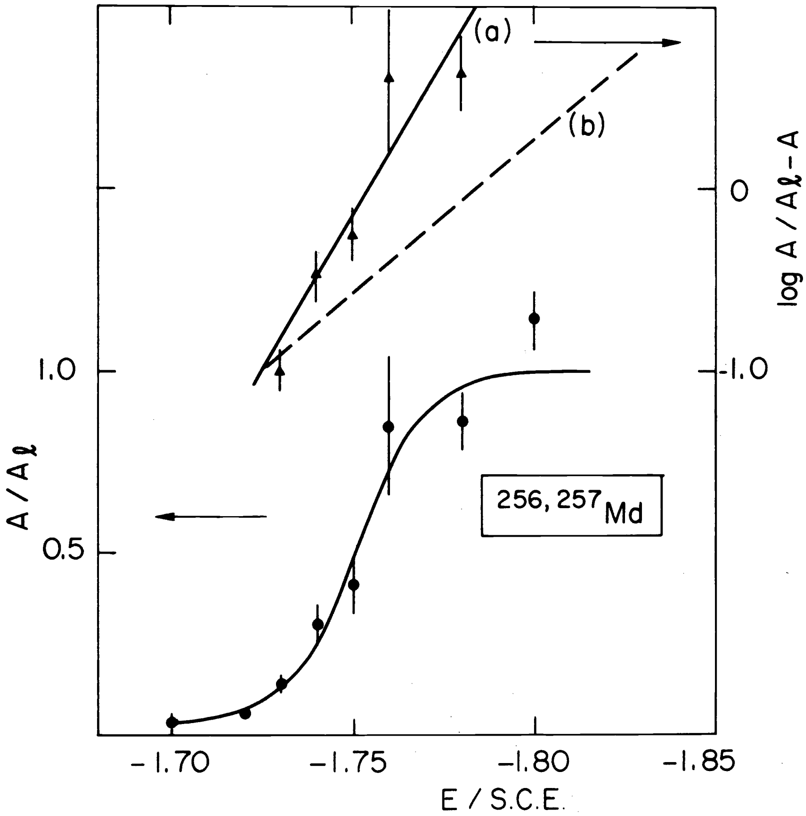

Fig. 4. Radiopolarogram and logarithmic transformed wave of Md in 0.1 M tetramethylammonium perchlorate, pH 2.4.

TRANSPORT NUMBER DETERMINATION OF LANTHANIDE AND ACTINIDE TRIVALENT IONS IN AQUEOUS SOLUTIONS.

In order to get a more complete view of the thermodynamics of the "Lanact" trivalent ions we are undertaking the study of hydration of these ions. The determination of the radius of the hydrated ions would be an important step toward the hydration study. We notice some attemps for the determination of the number of water molecule inside the first hydration sphere and calculations of hydration enthalpy (see for example : 10, 11, 12). However experimental data are scarce and semi theoretical treatment taking into account realistic coordination numbers of the ions are still lacking. Again radiochemical tracer experiments could be of interest for investigating heavy actinide ions. Moreover it should be interesting to get reliable correlations or semi theoretical expressions to get data for the complete actinide series. We are starting such works at the laboratory in both directions. I have to precise that the data I will mention now have to be considered as preliminary.

The measurement of diffusion coefficients D_i by the open-end capillary method (O.E.C.M.) as well as the mobility measurements by the technique of electrophoresis are in progress.

The use of radiochemical methods permits to get precise data by comparing internal standards even absolute measurements of u_i are much less precise than this of D_i. The obtained accuracy with the O.E.C.M. is 1 %.

Diffusion coefficient measurements

The theoretical expression of diffusion coefficient of ions is much similar to the extended Fuoss-Onsager expression of electrical conductance. It can be written :

$$D_i = D_i^o + S\,C^{1/2} + E\,C \log C + I_1\,C + I_2\,C^{3/2}$$

which is applicable when ions at the concentration C do not form pair associations.

At infinite dilution D_i^o is related to the mobility u_i^o by the Nernst-Einstein relation :

$$D_i^o/u_i^o = kT/|z|\,e$$

where z is the charge of the ion. Finally one deduces the stokes radius with the classical expression :

$$R_i = kT/6\pi\eta^o D_i^o$$

This is these radii we will compare for the lanthanide and actinide trivalent ions.

Lanthanide radii are calculated taking into account Spedding's measurements of conductances of chlorides (13).

Measurements of D_i for some lanthanide and actinide elements are now in progress at Orsay. Preliminary data have been obtained in collaboration with the Transuranium Research Laboratory (Oak Ridge), H. Latrous (Tunis University) and Orsay.

Europium and americium trivalent aqueous ions have very close D_i^o values ($D_i^o \sim 6\times10^{-6}$ cm^2/s) and therefore the R_i radii should be very close. This is consistent with the fact that cristallographic radii are similar : r (Eu^{3+}) = 1.07 Å and r (Am^{3+}) = 1.10 (CN = 8).

Otherwise first data obtained with californium and einsteinium seems to indicate that these elements have Stokes radii which are larger than those expected from lanthanide homologues. If this point is confirmed it would indicate an increasing of the coordination number of californium and einsteinium as compared with americium.

THERMOCHROMATOGRAPHY.

The identification of unusual compounds and oxidation states of actinides in the gaseous phase is one of the principal aims of the thermochromatography uses in our laboratory. The method initiated and developed at Orsay (14) was successfully applied at Dubna by Zvara and coworkers for studying the chemistry of the heaviest elements.

In this paragraph, I will present the experimental aspect of the method and recent data on tetrafluoride compounds of some actinides (15). The main purpose of the experiments is the study of einsteinium in order to see if this element could be observed at the tetravalent state. Many attempts have been performed to produce such oxidation state particularly at Oak Ridge by trying to prepare solid compounds.

Gas thermochromatography is derived from the gas solid chromatography. One studies the migration of a volatil compound inside a capillary tube in an atmosphere of flowing appropriate gas. A gradient of temperature is ensured throughout the tube and the compound is migrating by successive adsorptions and desorptions with the walls. The rate of migration decreases exponentially as the compound is reaching the cooler part of the tube. We define the characteristic temperature T_c of the deposition at the point of the column where the product is definitely deposited.

The experimental device is shown on fig. 5

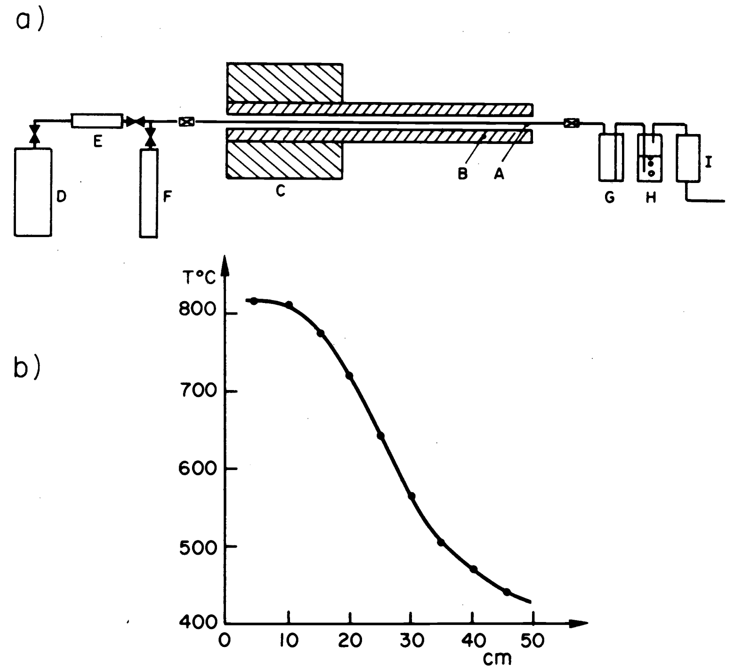

Fig. 5. a) Thermochromatograph :
A - Nickel tube ; B - Copper tube ; C - oven ; D - Fluorine bottle ; E - HF trap (KF) ; F - HF bottle ; G - Safety bottle ; H - Flowmeter ; I - Fluorine trap.

b) Temperature distribution.

One has a thickwall copper tubing of 50 cm length. The tube is heated at one extremity with a regulated oven and cooled at the other extremity at room temperature. Therefore an exponentially decreasing temperature is established throughout the tube.

In the axis of this tube, a 2 mm interior diameter nickel column is slided.

The gas (fluorine or hydrogen fluoride in these experiments) is allowed to flow at the rate of 1 cm/s from the highest temperature point toward the cooler region. On the extremity of a separate 1 mm diameter nickel stick, a 10^{-12} g (10^9 atoms) einsteinium sample was loaded. The stick was then introduced into the nickel tube so that the loaded einsteinium was located at the highest temperature point of the column. After the run, the stick was pulled out of the tube and the distribution of the deposited ^{254}Es was determined by measuring the 6.4 MeV activity at each cm portion of the stick.

The U.S. Department of Energy kindly supplied us with a stock solution containing ^{254}Es mixed with californium isotopes. After purification of the actinides by a cationic resin clean up column, ^{254}Es was then separated using a cationic aminex resin column. The elution with α-hydroxyisobutyrate at pH 3.9 is realized at 50° C. The total einsteinium fraction is separated in the first free columns of eluate and the remaining californium in the einsteinium fraction is less than 0.5 % by activity. In order to eliminate the ammonium α-hydroxyisobutyrate the einsteinium eluate is evaporated to dryness and calcinated. The residue is leached with 0.1 M HCl solution which is dropped and then dried on the extremity of the nickel stick for loading.

It was stated previously that for a given gas-solid system, and for a given series of transition elements such as actinides the temperature of deposition T_c varies sharply and linearly with the variation of valency state of the elements. This is shown on fig. 6, in case of tetravalent, pentavalent and hexavalent compounds. Observed deviations for different elements at the same oxidation state are less than 50° C but differences from one oxidation state to the other are more than 200° C. Therefore one can use the temperature T_c to characterize the oxidation state of an unknown compound. Tetrafluoride are supposed to be observed at 650° C ± 50° C and trivalent compound should have a T_c value too high (> 1000° C) to be experimentally observable since the nickel tube would be decomposed by the fluorine gas at such temperature.

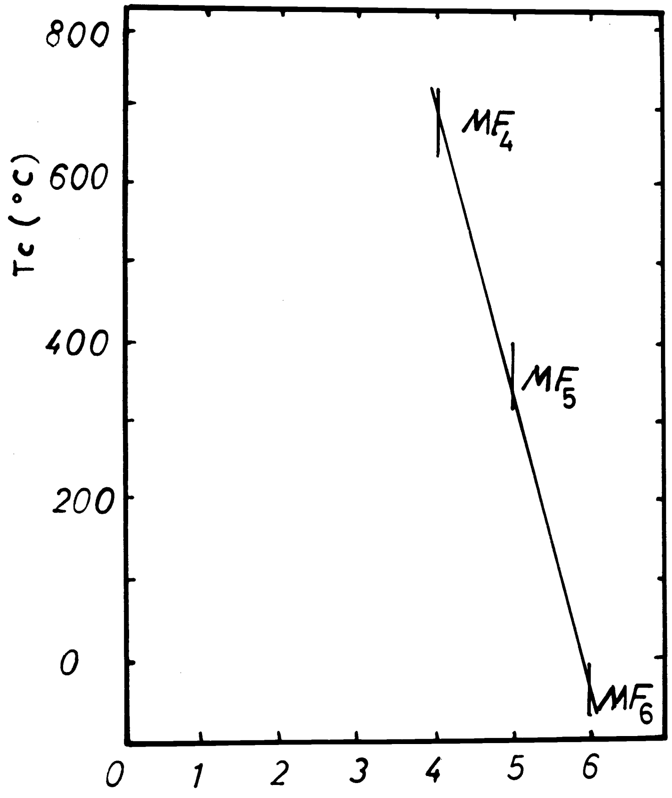

Fig.6 . Number of fluorine atoms in the molecule.

The einsteinium source was first heated progressively in the nickel tube in an HF gas flow. EsF_3 non volatile at the imposed temperature is formed. As soon as the temperature equilibrium is reached the fluorine is allowed to flow throught the column during 24 hours.

The fig. 7 shows the distribution of Es on the chromatograph. A peak of activity is observed at T_c = 695° C as well as a significant trail at higher temperature region of the tube.

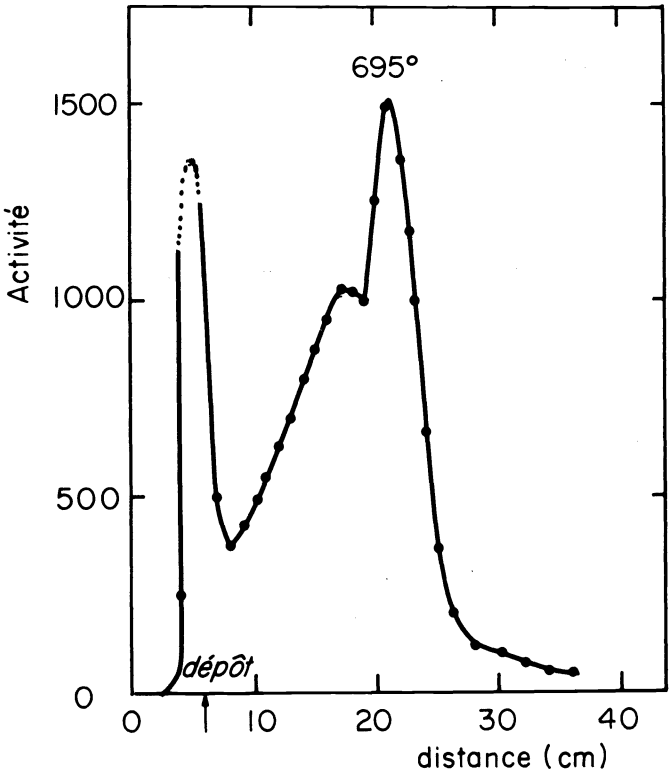

Fig. 7. Distribution of Es on the chromatograph tube.

This trail is due to the slow rate of formation of EsF_4 at the hot point. Consequently, a significant amount of Es remains at the hot point without migration even after 24 hours. The yield of volatilization of einsteinium compound is only 50 % for a hot point of 815° C and a 24 hours run. We noticed that the yield is decreasing for temperatures of the hot point above 815° C. It is 10 % with 835° C. This may be explained by a relative thermal unstability of EsF_4. The value of T_c for Es is compared in table 1 to those of Pu, Am, Cm, Bk and Cf tetrafluorides. For these last elements 100 % of the compound is volatilized from the hot point of 800° C after a 6 hour run.

The similar behavior in fluorine system of transuranium tetrafluorides and the einsteinium led us to conclude on the existence of gaseous EsF_4. In general the thermochromatographic technique ensures favorable conditions for stabilization of halides known to be unstable. According to recent work of Johansson on the stability of tetrahalides of f elements, EsF_4 would be unstable (16). The same statement is also valid for $PuCl_4$ and $CeCl_4$ which have not been produced yet as solid compounds. However these compounds as well as EsF_4 have been identified in the gaseous phase by thermochromatography.

Compounds	T_c Run duration 6 h °C	 20 h °C
PuF_4	630	616
AmF_4	690	640
CmF_4	713	691
BkF_4	698	664
CfF_4	700	662
EsF_4		695 *

* 24 hr run

Table 1. Experimental results

THERMODYNAMIC CONSEQUENCES OF ELECTROCHEMICAL STUDIES

Redox potentials

Redox potential E^o of the couple M^{3+}_{aq} /M(metal) are precisely determined for the lanthanides and for several of the light actinides from direct calorimetric measurements. With the radioelectrochemical data one can estimate half wave potential of reversible reduction and therefore one determined the amalgamation energy $\Delta_n = (E_{1/2})_{rev} - E^o$ (8).

It has been observed that Δ_n varies smoothly with the metallic radius in case of divalent and trivalent metals and consequently one has the possibility to estimate redox potential for several heavy actinides : Cf, Es, Fm, Md and No where the only experimental data are those obtained by radioelectrochemistry.

Another approach is to use the function P(M) proposed by Nugent, Burnett and Morss (17) to estimate the remaining unknown 3/0 redox potential since we noticed that this P(M) function varies linearly throughout the actinide series (18). By the same way it is also possible to estimate the unknown values of sublimation enthalpy ΔH_S using the smooth variation of the function $\Delta H^*_S(M) = \Delta H_S(M) + \Delta E(M)$ which was proposed by the same authors (17).

The knowledge of 3/0 redox potential for all the actinides permits to compare the stability of their different oxidation state X (X varying from 2 to 6) by plotting X time $E^o(M(X)/M)$ as a function of Z. These data are shown on fig. 8. Let me just remark that rough estimation of

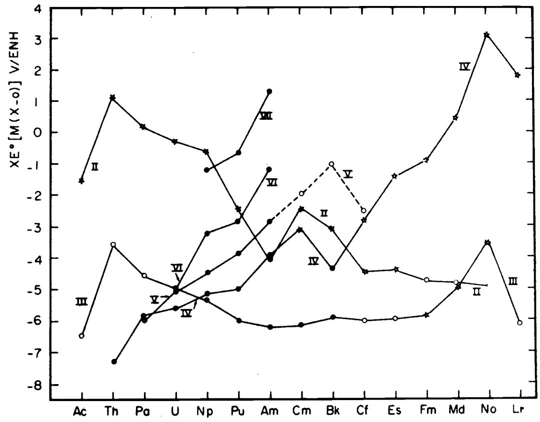

Fig. 8. Variations of XE° (M(X)/M) with Z for the oxidation state X = 2 to 6 for 5 f elements. ●, values deduced from experimental data reported in literature ; ✩, estimated data using results reported in (20) ; o, estimated data.

the stability of some unknown species could be done. For example one can predict that Cf(V) could exist in aqueous solution since it corresponds to a $5f^7$ half filled subshell configuration; the estimated $E^o(Cf(V)/Cf(IV))$ is around 0.3 V.

Hydration energy

If one consider a Born Haber cycle including the solid and gaseous metal, gaseous ionized atom and hydrated ion, it appears that sublimation enthalpy of the metal and formation enthalpy of the aqueous trivalent ion are now obtained or estimated for all the actinide series. Therefore, the knowledge of either ionization potential or hydration of ions would permits to deduce the fourth function.

Since no experimental data are available for the three first ionization potential of actinides we are interested in the determination of hydration enthalpy ΔH_h.

There is no analytical expression in the literature which gives with a good accuracy ΔH_h as a function of cristallographic radius r , charge z, hydration number n of the considered ion and with the radius r_w of water. For example, the calculated data by the expression given by Bockris and Reddy (19) fit well experimental data of halogenides and alkalis but the differences (ΔH_h) calculated - ΔH_h (deduced from experimental data) are very large by considering ions with charge +2, +3 or +4. They are 100 % deviations or more.

We develop a new expression of hydration which takes in account the classical terms : Born term $A = - a\, z^2/(r+2r_w)$, dipolar interaction $B = -b\,|z|\, n/(r+r_w)^2$, quadrupolar interaction $C = c\; z\;\; n/(r+r_w)^3$, induced dipole term $D = - d\; z^2\;\; n/(r+r_w)^4$ and I give an analytical expression for the interactions between central ion and the water molecules which are outside the first sphere of hydration : $W = w_0 + w_1\; z^2/(r+2r_w)^3$.

Since 37 ΔH_h data are available concerning ions of charge -1 to +4 : halogenides, alkalis, alkali-earths, trivalent and some divalent and tetravalent aqueous lanthanide ions, we compute the constants b, c, d, w_0, w_1 and the absolute hydration enthalpy of the proton. It is shown that the calculated ΔH_h gives less than 1 % standard deviation for the considered family of elements.

With the expression, ΔH_h has been computed for each M^{2+}, M^{3+} and M^{4+} ions of the lanthanide series. By considering the same hydration number n = 8 as for lanthanide ΔH_h could be also calculated for the M^{3+} actinide ions. But one notices previously that one needs more informations on hydration number. Therefore further calculations have to be undertaken with a better knoledge of the structure of the hydrated ions.

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