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The Complexity of Uranium(IV) Chloride, Bromide and Thiocyanate

STEN AHRLAND and RAGNAR LARSSON

Department of Inorganic and Physical Chemistry, Chemical Institute, University of Lund, Lund, Sweden

The complex chemistry of solutions of U(IV) has not been treated until recently and it must still be considered as rather undeveloped. It is significant that such a fundamental fact as the formula U^{4+} of the ion existing in strongly acid solutions was unequivocally established only a few years ago. As U(IV) no doubt merits the greatest attention, especially on account of its close resemblance to the four-valent states of the other actinides, a wider knowledge of its complex chemistry seems highly desirable. Towards this end the experimental difficulties which have largely caused the slow development up till now must be overcome. The solutions of U(IV) are thus easily oxidized by the air[1], they are heavily hydrolyzed even at very low pH[2,3], and even if the resultant difficulties could be mastered, it is not so easy to find a suitable method of measurement for the investigation of the complex systems.

SOME PREVIOUS INVESTIGATIONS ON U(IV) SOLUTIONS

Kraus and Nelson[2] have given the first decisive proof of the formula U^{4+} by measuring with the glass electrode the increase of acidity when known amounts of anhydrous UCl_4 are dissolved in acids of known concentration. It is found that considerably less than one mole of acid is liberated per mole of U(IV) dissolved. Thus a great part of U(IV) must remain in the unhydrolyzed state even in solution.

The formula U^{4+} could also be verified by measuring the influence of acidity on the potential of the U(VI)/U(IV) couple, as the species of U(VI) existing in acid solutions is certainly known[4] to be UO_2^{2+}. Several attempts have been performed to determine this effect of acidity. The earlier investigators[5-7] all used sulfate solutions, now known to be rather strongly complex[8-10] and measured, moreover, at varying ionic strength, employing very uncertain "degrees of dissociation" in their subsequent calculations. Their results are therefore not conclusive. A recent investigation[11] was performed using non-complex perchlorate solutions of constant ionic strength but the range of pH used was too narrow to allow a definite conclusion.

For the reasons mentioned the "normal potential" calculated from the measurements of sulfate solutions is a formal quantity, which is not identical with the real normal potential of the couple UO_2^{2+}/U^{4+}. This quantity has in fact quite recently been determined for the first time [12]. A value of 334 mV was obtained, which is $\approx$ 70 mV lower than that of the sulfate measurements, a consequence of the strong complexity of the sulfate system of U^{4+} in comparison with that of UO_2^{2+}.

As U^{4+} itself can exist only in strongly acid solutions, at least a preliminary knowledge of its hydrolysis is necessary for the investigation of any complex system of U(IV). The subject has first been studied by Kraus and Nelson [2] who measured extinctiometrically the concentrations of species of U(IV) in solutions of known $[H^+]$. They were able to explain all their data for $[H^+] > 20$ mC by one single equation of equilibrium, *viz.* $K_M = [H^+][UOH^{3+}]/[U^{4+}]$ where $K_M = 0.0278$ C at the ionic strength $I = 1.01$ C and the temperature 25° C. At lower $[H^+]$ the existence of higher, probably polynuclear, complexes must be postulated. In such solutions slow reactions are also observed undoubtly indicating a proceeding polymerization.

The number of experiments performed at a given I were, however, rather few, and the concentration of U(IV) was not varied greatly. The measurements, therefore, certainly do not permit a very elaborate theory, especially as the experimental errors are great.

A very thorough investigation has since been performed by Sillén and Hietanen [3]. Only measurements of $[H^+]$ were carried out, but this concentration as well as that of U(IV) were varied within very wide limits. The result is that the hydrolysis must involve merely polynuclear complexes, presumably of the general formula $U(UOOH)_n^{n+4}$ which may mean a chain complex resembling the chains proved [13] in crystals of basic uranium(IV) sulfate *.

In addition to the hydrolysis, only two complex systems of U^{4+} seem to have been investigated before. From a comparison between the hydrolysis of perchlorate and chloride solutions, Kraus and Nelson [2] estimated a thermodynamic complexity constant = 7.0 C^{-1} for UCl^{3+}, provided the given form of the Debye-Hückel law is obeyed. This value would correspond to 0.5 C^{-1} at $I = 1$ C. Such a calculation is, of course, very uncertain, but in any case the chloride system must be very weakly complex.

Betts and Leigh [9] have investigated the sulfate system, using the extraction method of Connick and Mc Vey [15]. As the concentration of U(IV) extracted into the benzene phase is approximately a function of only one unknown variable, *viz.* $[U^{4+}]$, the method is equivalent to a determination of the concentration of the free central ion. Methods for the evaluation of complexity

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* According to Sillén, the hydrolytic reactions of a great number of metal ions are of this exclusively polynuclear type. Also the measurements of one of the present authors [14] on UO_2^{2+} can be surprisingly well fitted into this scheme. As the interpretation tentatively presented before was dependent on rather uncertain extrapolations leading to limiting values which could hardly be reasonably explained, this new approach is likely to hold a greater part of the truth than the previous one.

constants from such measurements have been given by Bjerrum [16], Leden [17] and Fronaeus [18]. By applying these general methods, Sullivan and Hindman [10] were able to correct the erroneous values of the constants calculated by the original authors.

PLAN OF THE PRESENT INVESTIGATION

The method most readily available for a determination of the complexity of an U(IV) system is undoubtly measurements of the redox potential of the UO_2^{2+}/U^{4+} couple in solutions of known acidity and known total concentrations of U(VI) and U(IV), containing varying amounts of the ligand. If the complexity of the U(VI) system is known, all complexity constants of the U(IV) system may be calculated from the differences between the potentials of complex and non-complex solutions as will be shown below.

The U(VI)/U(IV) redox potential is sensitive to light in the presence of certain anions, *e. g.* sulfate [6,19], while other ions, *e. g.* chloride [19], have no effect. It is therefore advisable to investigate for every system measured whether its redoxpotentials are affected by illumination.

A couple of complications may arise owing to the existence of two states of oxidation in the solutions. Thus mixed polynuclear complexes may be formed containing both UO_2^{2+} and U^{4+} (*cf. e. g.* Mc Connell and Davidson [20]). The possibility must in any case be considered by our method of calculation.

Further, a mixture of U(VI) and U(IV) can react forming U(V)[21]. If this happens the total concentrations of U(VI) and U(IV) are no longer known and the new complex-forming species UO_2^+ is, moreover, formed. The equilibrium between the reacting components is, however, highly dependent on $[H^+]$, and in strongly acid solutions U(V) is formed only in quite negligible amounts [21]. A complex formation ought to diminish the relative amount of U(V) further, as UO_2^+ can be anticipated to have a lower complex-forming power than UO_2^{2+} and U^{4+} on account of its lower charge. As to the hydrolysis, this anticipation has also been experimentally verified [2,21,14].

As is often the case in redox measurements, the potential of the present couple reaches its value of equilibrium very slowly if no special measures are taken. As a great number of measurements are desired here in a reasonable period of time, a way of accelerating the adjustment of the potential must be found. This problem has often been successfully solved by the addition of a mediator system.

Generally all substances may serve as mediators which rapidly give a stable redox potential, even if present in very low concentrations. In order that a mediator may be able to adjust the potential of a given system some additional conditions must, however, be fulfilled, which in practice highly reduce the number of mediators effective in a certain case (Luther [22]). First, the two systems present must be able to react mutually so that a real redox equilibrium is rapidly established. It must further be possible to choose the concentrations of the components of the main system so much higher than those of the mediator that they are only slightly altered by the redox reaction. Preferably this alteration should be so slight that the differences of potential used in our calculations are not at all affected by the mediator present, but in every case it must be possible to arrive at such a value of the differences by measuring at several concentrations of the mediator, subsequently extrapolating to zero. In this way the mediator only communicates a potential to an immersed inert electrode without affecting it. In order that a well-defined potential shall really be transferred it is, however, also necessary that the ratio between the concentrations of the components of the mediator system does not assume too extreme values in the solutions measured. For a given redox potential, this ratio is determined by the normal potential and pH-dependence of the mediator, the values of which must, therefore, be considered in the first place in the search for a suitable system.

All the present measurements are performed in a strongly acid medium, having $[H^+] = 600$ mC throughout, in order to prevent the disturbance of the complex formation of U^{4+} by hydrolytic reactions. According to the investigations [2,3] mentioned above such a $[H^+]$ implies a degree of hydrolysis of ≈ 4 % in a perchlorate medium of the ionic strength $I = 1$ and the temperature 20° C, *i. e.* under the conditions of the present measurements. Perhaps a still lower value would have been desirable, but an increase of $[H^+]$ would presuppose an increase of I too. This is out of the question, as the determinations [23,24] of the corresponding uranyl systems utilized here all refer to $I = 1$. For the same reason, the temperature must be retained at 20° C.

It is true that the present medium is, nevertheless, not identical with that of the uranyl measurements, as a considerable part of the sodium ions have been exchanged for hydrogen ions. The constants of the uranyl systems determined previously are, therefore, only approximately valid here. But as may be anticipated on account of the difference of charge, U^{4+} forms much stronger complexes than UO_2^{2+} with a certain ligand. The complexity of UO_2^{2+} is, therefore, in fact only a correction applied in the calculation of the corresponding system of U^{4+}. For this purpose the values at hand are considered as sufficiently correct. The truth of this assumption is moreover tested as described later on.

The redox potential E_H of a perchlorate solution having $[UO_2^{2+}]/[U^{4+}] = 1$ and $[H^+] = 600$ mC is presumably ≈ 310 mV. Among mediators known, only the systems indigosulfonate / leukoindigosulfonate [25] seem to have suitable values of the ratio between their oxidized and reduced forms in such solutions. As to the system selected for closer examination, *viz.* indigotetrasulfonate(-5,7,5′,7′) / leukoindigotetrasulfonate, this ratio is indeed only ≈ 0.03 at $E_H \approx 310$ mV, but on account of the general tendency of U^{4+} to form complexes stronger than those of UO_2^{2+}, E_H will rise in connection with the complex formation and hence the ratio too. Its optimal value of 1 corresponds to $E_H \approx 355$ mV.

The mediator selected possesses two —NH— groups which probably means that it has a strong complex-forming ability. As its two components have the same coordinating groups they ought, however, to give complexes of about the same strength. Then the ratio between their concentrations remains about the same and the mediator may thus still be used in the potential range previously calculated. On the other hand, complex formation of the mediator must of course alter the ratio $[UO_2^{2+}]/[U^{4+}]$, as UO_2^{2+} and U^{4+} certainly have very different affinities also towards this ligand. The effect is, however, removed by the extrapolation to zero concentration of the mediator earlier described (p. 140).

It must be emphasized that redox potentials obtained by the use of a mediator must, nevertheless, be proved to be really identical with those found without a mediator. This may sometimes be ascertained by direct comparison if the adjustment is not too slow without a mediator. Another good criterion is that the potential must vary according to Nernst's law when the ratio $[UO_2^{2+}] / [U^{4+}]$ is varied in a known manner as can be brought about in non-complex solutions.

For the sake of simplicity, only anions of strong acids are selected as ligands for the present investigation, *viz.* chloride, bromide and thiocyanate ion. Only in this way the acidity can be kept quite constant which facilitates both experimental work and calculations. Moreover the free concentration [A] of such ligands may be raised to high values even in acid solutions, and hence it is possible to follow the complex formation within a wider concentration range.

CALCULATION OF THE COMPLEXITY CONSTANTS FROM THE POTENTIALS MEASURED

Experimentally the emf E of cells of the following type is measured:

+ Au	10.06 mC $HClO_4$ 990 mC $NaClO_4$ quinhydrone(s.)	1 C $NaClO_4$	C_M mC U(VI) C_L mC U(IV) C_A mC ligand C_I mC mediator $[H^+] = 600$ mC; $I = 1$	Au —

where C_M, C_L, C_A and C_I thus are the total concentrations of U(VI), U(IV), ligand and mediator respectively.

E is composed according to the following formula:

$$E = E_{RE} + E_d — E° — \frac{2RT}{F} \ln [H^+] — \frac{RT}{2F} \ln \frac{f_M f_H^4}{f_L} — \frac{RT}{2F} \ln \frac{[M]}{[L]} \qquad (1)$$

where

E_{RE} = potential of the reference electrode
E_d = sum of liquid junction potentials
E^0 = normal potential of the UO_2^{2+}/U^{4+} couple; $[L] = [U^{4+}]$; $[M] = [UO_2^{2+}]$
f_H, *etc.* = activity coefficient of the ion indicated by the subscript.

As $[H^+]$ and I are kept constant, it is assumed that E_d and the coefficients f are constant too, and thus (1) may be written as

$$E = E_k — \frac{RT}{2F} \ln \frac{[M]}{[L]} \qquad (2a)$$

where E_k is the (unknown) sum of the constant terms. It is eliminated by measuring E $(= E')$ of a cell having $C_A = 0$ in the right half-cell. Then [M] and [L] are identical with the known stoicheiometric concentrations of U(VI) and U(IV) which for this particular solution are denoted by C'_M and C'_L. Hence

$$E' = E_k - \frac{RT}{2F} \ln \frac{C'_M}{C'_L} \tag{2b}$$

and

$$E' - E = E_{LM} = \frac{RT}{2F} \ln \frac{[\mathrm{M}]}{[\mathrm{L}]} \cdot \frac{C'_L}{C'_M} \tag{3}$$

The ratio between the total concentrations of U(VI) and U(IV) is always kept constant during a series of measurement, *i. e.* $C'_L/C'_M = C_L/C_M$.

There do not exist any polynuclear complexes M_mA_n, but the possible existence of mixed complexes has to be considered. They may be represented in the sequel by their simplest type MLA_q. Thus it is valid for the total concentration of U(VI):

$$C_M = [\mathrm{M}](1 + \sum_{n=1}^{N} \beta_n[\mathrm{A}]^n + [\mathrm{L}]\sum_{q=1}^{Q} \delta_q[\mathrm{A}]^q) \tag{4}$$

where

$$\beta_n = [\mathrm{MA}_n] \,/\, [\mathrm{M}][\mathrm{A}]^n \text{ and } \delta_q = [\mathrm{MLA}_q] \,/\, [\mathrm{M}][\mathrm{L}][\mathrm{A}]^q$$

As to U(IV) there may exist polynuclear complexes $\mathrm{L}_l\mathrm{A}_p$ in addition to the mononuclear and mixed series. In the following formula of the total concentration of U(IV) this possibility is taken into account by the introduction of terms belonging to the dinuclear complexes $\mathrm{L}_2\mathrm{A}_p$:

$$C_L = [\mathrm{L}](1 + \sum_{p=1}^{P'} \gamma'_p[\mathrm{A}]^p + [\mathrm{L}]\sum_{p=1}^{P''} \gamma''_p[\mathrm{A}]^p + [\mathrm{M}]\sum_{q=1}^{Q} \delta_q[\mathrm{A}]^q) \tag{5}$$

where

$$\gamma'_p = [\mathrm{LA}_p] \,/\, [\mathrm{L}][\mathrm{A}]^p \text{ and } \gamma''_p = [\mathrm{L}_2\mathrm{A}_p] \,/\, [\mathrm{L}]^2[\mathrm{A}]^p$$

The expression of C_L/C_M $(= C'_L/C'_M)$ obtained from (4) and (5) gives when inserted in (3):

$$E_{LM} = \frac{RT}{2F} \ln \frac{1 + \sum\limits_{p=1}^{P'} \gamma'_p[\mathrm{A}]^p + [\mathrm{L}] \sum\limits_{p=1}^{P''} \gamma''_p[\mathrm{A}]^p + [\mathrm{M}] \sum\limits_{q=1}^{Q} \delta_q[\mathrm{A}]^q}{1 + \sum\limits_{n=1}^{N} \beta_n[\mathrm{A}]^n + [\mathrm{L}] \sum\limits_{q=1}^{Q} \delta_q[\mathrm{A}]^q} \tag{6}$$

From (6) it is concluded:

a. E_{LM} is a function of [A] only, if only mononuclear complexes exist.
b. E_{LM} is a function of [A] and [L] if polynuclear complexes of U(IV) are present.
c. If mixed complexes are formed, E_{LM} is a function of [A], [L] and [M].

For the sake of simplicity, the following notation is now introduced:

$$1 + \sum_{n=1}^{N} \beta_n [\mathrm{A}]^n = X_M \qquad (7a) \qquad\qquad 1 + \sum_{p=1}^{P'} \gamma'_p[\mathrm{A}]^p = X_L \qquad (7b)$$

$$\sum_{p=1}^{P''} \gamma''_p[\mathrm{A}]^p = Y_L \qquad (7c) \qquad\qquad \sum_{q=1}^{Q} \delta_q[\mathrm{A}]^q = Z \qquad (7d)$$

Even if polynuclear complexes exist, *i.e.* $Z \neq 0$ and / or $Y_L \neq 0$, the constants γ'_p of the mononuclear series would still be computed according to a method of extrapolation, analogous to that advanced by Fronæus [18] for solutions containing one central ion. One would then measure E_{LM} as a function of C_A at decreasing values of C_M and C_L keeping the ratio between them constant. By cutting the functions thus found at constant E_{LM}, C_A is obtained as a function of C_L (or C_M). By extrapolation to $C_M = C_L = 0$, $\lim C_A = [\mathrm{A}]$ is found, while E_{LM} simultaneously takes the form

$$E_{LM} = \frac{RT}{2F} \ln \frac{X_L}{X_M} \qquad (8)$$

where X_M is known from the uranyl measurements. From (8) X_L corresponding to the found [A] may thus be calculated and hence γ'_p according to the usual method (*cf.*[26 p. 787]).

Unfortunately this straightforward method cannot be well applied here as the redox potentials, even in the presence of a mediator, do not adjust themselves properly at the lowest values of C_L and C_M which must be used to secure a good extrapolation. Moreover, the mediator then affects the ratio C_L/C_M rather seriously.

Therefore the method must be so modified that first only $C_L \rightarrow 0$ whereas C_M is kept at a high value. An extrapolation to $C_L = 0$ at constant E_{LM} then gives

$$\lim_{C_L \rightarrow 0} C_A = [\mathrm{A}] + \bar{n} \cdot C_M \qquad (9)$$

where $\bar{n}$ is the ligand number of the uranyl system at the prevailing [A]. These quantities are easily found from (9) and the known complex formation function of the uranyl system. The computation is conveniently performed graphically, the corresponding values of ($\bar{n}$, [A]) sought for being obtained as the point of section between the straight line (9) and the formation curve.

By this extrapolation, E_{LM} takes the form

$$E_{LM} = \frac{RT}{2F} \ln \frac{X_L + [\mathrm{M}] \cdot Z}{X_M} \qquad (10)$$

which does not permit a direct calculation of X_L if $Z \neq 0$. If it is preliminarily assumed however that $Z = 0$, then corresponding values of X_L and [A] are known and hence γ'_p may be calculated as before.

The assumption $Z = 0$ is then immediately put to an experimental test by measuring E_{LM} as a function of C_A at decreasing C_M whereas C_L is kept at a high value. An extrapolation analogous to the preceding one gives

$$\lim_{C_M \to 0} C_A = [\mathrm{A}] + \overline{m} \cdot C_L \tag{11}$$

where $\overline{m}$ is the ligand number of the uranium(IV) system preliminarily known as a function of [A] from the constants γ'_p just determined. From (11), [A] may thus be calculated.

In this case E_{LM} has the form

$$E_{LM} = \frac{RT}{2F} \ln \frac{X_L + [\mathrm{L}] \cdot Y_L}{X_M + [\mathrm{L}] \cdot Z} \tag{12}$$

As seen, a finite value of Z influences (10) and (12) in quite different ways, and (12) is, moreover, also dependent on Y_L.

If now the values of X_L (or possibly $X_L + [\mathrm{M}] \cdot Z$) calculated from (10) are inserted for the numerator of the fraction of (12) and the denominator then computed and found to be the same function X_M as determined before in the uranyl measurements, the only reasonable explanation is that the functions (10) and (12) are in reality identical. This implies that $Z = Y_L = 0$, *i. e.* no polynuclear complexes exist whatsoever. In addition, it must then also be concluded that the function X_M remains unchanged at the qualitative change of medium made between the two determinations of it.

This method of determination compulsorily chosen thus affords a good test of the existence of polynuclear complexes as well as of the effect of the medium change. Its weakness lies in that it cannot be used at all if the test really indicates that polynuclear complexes are presumably formed.

Finally it should be pointed out, that this method of calculation may be greatly simplified when a system is only weakly complex. In such a case, $C_A \approx [\mathrm{A}]$ in all solutions and no extrapolations are thus necessary to obtain the values of [A]. Then the criterions a—c p. 142 may be at once applied. If only mononuclear complexes are indicated, X_L may be directly calculated from (8).

EXPERIMENTAL

Chemicals used: Uranium (IV) perchlorate was prepared by cathodic reduction of a strongly acid solution of uranyl perchlorate, a method originally worked out by Rosenheim and Loebel [27]. A mercury pool, about 6 cm in diameter, covering the bottom of a Pyrex beaker served as cathode. It is connected with the outer circuit by a platinum wire, the part of which passing through the solution surrounded by a plastic tube. The anode compartment, containing $\approx$1 C perchloric acid, consisted of a glass tube ending in a sintered glass disc. In the tube a platinum wire was inserted as the anode.

The cathodic solutions contained a concentration of uranium $\approx$0.1 C, and a $[\mathrm{H}^+]$ $\approx$1.5 C. If then a voltage of 12 V was applied a current $\approx$0.7 A resulted. The completion of the reaction was indicated by an incipient formation of U(III), whose deep red colour when mixed with the green one of U(IV) turned the solution almost black. The simultaneous formation of hydrogen was rather slight on account of its great overvoltage towards the mercury electrode.

All U(III) formed was oxidized by aeration of the solution for one minute. It was then immediately transferred into a bottle where it could be stored under a permanent

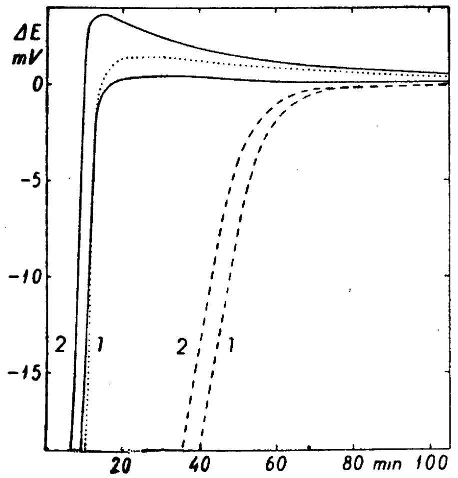

Fig. 1. The difference ΔE between the emf measured and its final value of equilibrium E' as a function of the time elapsed from the mixing of S. Fulldrawn, dotted and dashed curves refer to $C_M : C_L = 30 : 30$, $10 : 30$ and $30 : 10$ respectively. The values of C_I of the curves are given by the numbers attached to them.

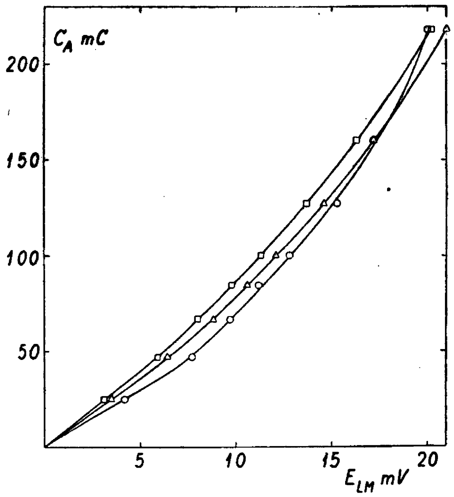

Fig. 2. The connection between E_{LM} and C_A in the thiocyanate system. The experimental points of the series of $C_M : C_L = 30 : 30$, $10 : 30$ and $30 : 10$ are denoted by squares, triangles and circles respectively.

overpressure of electrolytically prepared hydrogen, freed from oxygen according to Meyer and Ronge [28]. The bottle was equipped with a burette which permitted withdrawal of known portions of the solution without letting air into the stock.

This stock solution first had to be analysed for U(IV) and U(VI), the latter formed by the oxidation of U(IV) which could be hardly avoided in the long run. In fact there was no point in endeavouring to eliminate this oxidation completely, as a small contamination of U(VI) in the solution is quite harmless, provided its concentration is known.

C_L of the stock solution was determined by direct cerimetric titration, using ferroin (tri-*o*-phenantroline iron(II) sulfate) as an indicator. A similar titration on another sample which had first been reduced by the cadmium reductor gave $C_L + C_M$. The difference between the titrations thus yielded C_M. It was found that the solution keeps very well under the arrangement described even if portions are often withdrawn. C_L decreased by only by ≈ 0.8 % in one month while $C_L + C_M$ then remained constant.

Finally, the solution of U(IV) also had to be analyzed for $[H^+]$. This cannot be performed by direct alkalimetric titration on account of the acid properties of U^{4+}. Nor is it possible to measure $[H^+]$ potentiometrically with the high accuracy of ≈ 0.5 %, necessary owing to the strong influence of $[H^+]$ on E (*cf.* (1)). The method successfully employed here utilizes cation exchange. A sample was passed through a column of Amberlite in its hydrogen form. All U^{4+} and UO_2^{2+} were then exchanged for H^+. The solution leaving the column may therefore be titrated in the usual way. If a total concentration of acid $= [H^+]_t$ is found then the original $[H^+] = [H]_t - 4\,C_L - 2\,C_M$.

The uranyl perchlorate was prepared as decribed previously [14]. The present preparation did not contain any excess or deficit of perchloric acid (*cf* [14] p. 384). A stock solution of $C_M \approx 1/3$ C was prepared, whose exact concentration was cerimetrically determined $= 337$ mC.

Tab. 1. The chloride system, $C_I = 1$ *mC*

$\gamma_1 = 2.0 \pm 0.5$ C^{-1}

C'_M mC →	30	30	10	mean E_{LM} mV	X_M	X_L	X_{1L} C^{-1}
C'_L mC →	30	10	30				
C_A mC	E_{LM} mV						
67.5	0.9	0.9	0.8	0.9	1.054	1.132	1.95
117	1.4	1.5	1.4	1.4	1.094	1.222	1.90
166	1.9	1.9	1.8	1.9	1.133	1.317	1.91
210	2.3	2.3	2.3	2.3	1.168	1.402	1.92
250	2.7	2.6	2.8	2.7	1.200	1.486	1.95
315	3.5	3.2	3.7	3.5	1.252	1.651	2.07
400	4.5	4.0	4.7	4.4	1.320	1.870	2.18
500	5.3	4.8	5.9	5.3	1.400	2.130	2.26

The *perchloric, hydrochloric* and *hydrobromic acids* were of analytical grade, as well as the *sodium salts* used. The concentrations of the stock solutions of the last-mentioned were checked by ion exchange and subsequent alkalimetric titration.

The *sodium indigotetrasulfonate* used had been obtained from I. G. Farben. A solution of $C_I = 25$ mC appeared to be quite stable, whereas a precipitate was gradually formed when $C_I = 100$ mC.

Procedure. At the outset, the right half-cell of p. 141 contained a known volume of a solution S having $C_L = 10$ or 30 mC, $C_M = 10$ or 30 mC and $C_I = 1$ or 2 mC, according to the schemes given in the Tables 1—3. S was prepared directly in the electrode vessel from the stock solutions of U(IV), U(VI) and the mediator, and then perchloric acid and sodium perchlorate were added so that $[H^+] = 600$ mC and $I = 1$ C. Immediately after the preparation of S, a bubbling of purified [26] nitrogen gas through the solution was started and then maintained during the whole series of measurement.

Tab. 2. The bromide system. $C_I = 1$ *mC*

$\gamma_1 = 1.5 \pm 0.5$ C^{-1}

C'_M mC →	30	30	10	mean E_{LM} mV	X_M	X_L	X_{1L} C^{-1}
C'_L mC →	30	10	30				
C_A mC	E_{LM} mV						
67.5	0.9	0.7	0.8	0.8	1.033	1.100	1.48
117	1.4	1.3	1.4	1.4	1.059	1.183	1.56
166	1.8	1.9	2.0	1.9	1.083	1.259	1.56
210	2.3	2.5	2.4	2.4	1.105	1.336	1.60
250	2.8	3.0	2.9	2.9	1.125	1.416	1.67
315	3.6	3.6	3.5	3.6	1.158	1.540	1.72
400	4.6	4.3	4.5	4.5	1.200	1.714	1.78
500	5.6	5.5	5.7	5.6	1.250	1.947	1.90

Tab. 3. The thiocyanate system. — Determination of E_{LM} as a function of C_A including the extrapolation to $C_I = 0$.

$C'_M \rightarrow$ mC	30			30			10		
$C'_L \rightarrow$ mC	30			10			30		
$C_I \rightarrow$ mC	2	1	0	2	1	0	2	1	0
$E' \rightarrow$ mV	301.7	304.2	306.7	285.0	287.9	290.8	314.0	317.5	321.0
C_A mC	E_{LM} mV								
25.1	3.0	3.1	3.1	4.0	4.1	4.2	3.4	3.5	3.5
47.0	5.9	5.8	5.9	6.7	7.2	7.7	6.5	6.4	6.4
66.7	8.0	8.0	8.0	8.8	9.3	9.7	8.8	8.8	8.8
84.2	9.9	9.7	9.8	10.4	10.8	11.2	10.5	10.7	10.6
100	11.4	11.2	11.3	11.8	12.3	12.8	12.1	12.1	12.1
127	13.9	13.5	13.7	13.8	14.6	15.3	14.6	14.6	14.6
160	16.6	16.1	16.3	16.0	16.6	17.2	17.2	17.2	17.2
218	20.4	20.0	20.2	19.5	19.8	20.0	20.9	21.0	21.0

The course of the emf of the cell formed was then observed. As the mediator was added in its oxidized form, S exhibited a high redox potential, and the emf therefore started at a low value (*cf* (1)). It rose, however, very quickly indicating the rapid progress of the redox reaction in the solution, also manifested by the bleaching of the indigo colour. After 1.5—4 hours, the length of time being dependent on C_L, C_M and C_I of S, the emf asymptotically reached the steady value E' of the redox equilibrium. If the reaction first proceeded very rapidly the emf described a damped oscillation about E' as seen from Fig. 1. In such a case a longer time was required for the definitive attainment of E' than if the reaction started at a lower rate. A certain E' could, as a rule, be reproduced within 1 mV.

After E' had been reached portions of a ligand solution T were added from a burette. In the chloride and bromide measurements T had $[H^+] = 600$ mC. As to thiocyanate, strongly acid solutions are not stable[29] and, therefore, ligand and acid were in this case added separately so that the resulting cell solution still retained $[H^+] = 600$ mC.

In the beginning of each series the emfs E adjusted themselves within ≈ 10 minutes, but with increasing C_A a longer time was required, at last up to more than half an hour. Simultaneously the reproducibility of the difference E_{LM} decreased from ≈ 0.2 mV to 0.5—1.0 mV. As a rule two parallel runs were made for every series.

Once reached, a value of E' or E, and thus E_{LM} too, showed no drift, indicating that the arrangements made were really able to prevent an appreciable oxidation by the air during the time of measurement. Nor was E' or E in any case affected by a change of the illumination, *e. g.* from darkness to ordinary daylight. None of the systems investigated here are thus sensitive to light.

The values of E' given in Table 3 are obviously dependent on C_I. The comparison intended between E' determined at different values of C_M/C_L must, therefore, be made with values of E' valid at $C_I = 0$. The extrapolation is performed in Table 3. The resulting difference of E' between $C_M/C_L = 1$ and 3 is 15.9 mV, between 1 and 1/3 14.3 mV which within the limits of experimental error agree with the value of 13.9 mV expected

Tab. 4. Determination of the complexity of the thiocyanate system of uranium(IV).

$\gamma_1 = 31 \pm 2\ C^{-1}$ $\gamma_2 = 90 \pm 30\ C^{-2}$ $\gamma_3 \approx 150\ C^{-3}$

C'_L mC	30		10		0					
E_{LM} mV	C_A mC	C_L mC	C_A mC	C_L mC	C_A mC	C_M mC	[A] mC	X_M	X_L	X_{1L} C^{-1}
4.0	32.5	27.6	23.3	9.44	18.5	28.6	16.0	1.092	1.499	31.2
7.0	56.8	25.7	41.9	8.95	33.9	27.5	29.6	1.174	2.044	35.3
10.0	86.2	23.6	69.3	8.28	60.2	25.5	53.6	1.324	2.922	35.9
13.0	119.0	21.1	101.9	7.45	92.6	23.1	83.8	1.525	4.270	39.0
15.0	143.0	19.3	125.4	6.88	115.6	21.4	105.7	1.680	5.510	42.8
17.0	169.3	17.3	155.5	6.10	148.0	18.9	137.1	1.923	7.387	46.6
20.0	213		213		213		213	2.606	12.71	55

according to (2b). E' calculated in this way thus seems to be determined solely by the uranium system, which is also confirmed by some measurements performed without the mediator, giving approximately the same E' as above.

As expected from a comparison between (2b) and (3), E_{LM} proves to be much less dependent on C_I than E' is. From Table 3 it is seen that C_I has a pronounced influence only in the series of $C_L = 10$ mC, whereas in the other series no systematic deviation occurs when C_I is changed from 1 mC to 2 mC. Therefore an extrapolation to $C_I = 0$ has to be performed only for the series of $C_L = 10$ mC, while for the other series E_{LM} at $C_I = 0$ is taken as the mean between the values determined at the two C_I used.

Even for the series of $C_L = 10$ mC, the influence of C_I is very slight at the lowest C_A. As to the chloride and bromide systems E_{LM} reaches only very low values, Tables 1 and 2. It is then concluded that a variation of C_I is quite unnecessary in the determination of these systems.

Tab. 5. Determination of corresponding values of X_M and [A] of the uranyl thiocyanate system from the results obtained for the uranium(IV) system. — Comparison between the X_{1M} hence calculated and those found previously[24].

C'_M mC	30		10		0						
E_{LM} mV	C_A mC	C_M mC	C_A mC	C_M mC	C_A mC	C_L mC	[A] mC	X_L	X_M	X_{1M} C^{-1}	ext. X_M C^{-1}
3.0	24.9	28.1	21.5	9.47	19.8	28.5	11.8	1.379	1.088	7.4	5.8
6.0	48.2	26.4	43.6	8.91	41.3	26.9	27.4	1.920	1.195	7.1	5.9
8.5	71.5	24.6	64.0	8.40	60.1	25.5	42.8	2.504	1.278	6.5	6.0
10.0	86.2	23.5	78.6	8.04	74.7	24.4	55.7	3.034	1.374	6.7	6.0
12.0	107.8	21.9	99.0	7.53	94.4	22.9	73.8	3.826	1.480	6.5	6.2
14.0	130.7	20.2	120.7	6.98	115.4	21.4	93.8	4.820	1.592	6.3	6.4
17.0	169.3	17.3	158.0	6.05	151.9	18.6	130	6.880	1.791	6.1	6.7
20.0	214.0	14.0	202.0	4.95	195.4	15.3	176	10.06	2.065	6.1	7.2

RESULTS

As seen from Tables 1 and 2, the low values of E_{LM} in the chloride and bromide systems are, moreover, independent of C_L and C_M. This implies a very weak and solely mononuclear complex formation. The calculations could therefore be performed according to the simplified method given above, postulating $C_A \approx [\mathrm{A}]$. The functions X_{1L} thus found increase very slowly for both systems. Only the first complex can, therefore, be considered as definitely proved, while the slight increase of X_{1L} may be attributed to a change of the activity coefficients as well as to a formation of a weak second complex. This difficulty is common to all determinations of constants of complexes higher than the first one, as it is then necessary to exchange a considerable part of the perchlorate ions of the medium for ligand ions. The values of γ_1, with estimated experimental errors are given in Tables 1 and 2.

It is evident from Table 3 and Fig. 2 that the complexity of the thiocyanate system is so strong that the complete method of computation must be applied. Thus corresponding values of X_L and [A] are first calculated according to (9) and (10) on the presumption that no polynuclear complexes exist, Table 4. For this the curves of $C_M{:}C_L = 30 : 30$ and $30 : 10$ of Fig. 2 are used. At the highest C_A, the curves seem to meet though the difference between C_A and [A] must still be rather considerable judging from the previous values of Table 4. One cause of this anomalous behaviour is, no doubt, the great unreliability of the highest E_{LM}, as illustrated by their poor reproducibility, but the full explanation is still obscure. For the last row of Table 4, the approximation $C_A \approx [\mathrm{A}]$ is therefore used.

The course of X_{1L} indicates the existence of at least the first two mononuclear complexes, but a still closer agreement with the experimental points is obtained if also the third complex is postulated. Its constant could be only very roughly calculated and the computation is, of course, very uncertain on account of the changes of activity discussed above. The values of γ_p are found in Table 4.

The test of the assumptions made is then performed, using the curves of $C_M{:}C_L = 30 : 30$ and $10 : 30$ of Fig. 2. The resulting values of [A], X_M and hence X_{1M} are found in Table 5, the last column of which also contains the values of X_{1M} extinctiometrically determined before [24]. A surprisingly good agreement exists between the two sets of X_{1M}, especially if the considerable differences in medium as well as in experimental method are considered. A value of $\beta_1 = 6.5 \pm 1\ \mathrm{C}^{-1}$ is determined here which should be compared with $\beta_1 = 5.7 \pm 0.3\ \mathrm{C}^{-1}$ obtained before. The higher complexes of the extinctiometric investigation are on the other hand not found here. Their concentrations at the present values of [A] are however rather slight, and the calculation of these higher constants are, as repeatedly pointed out, much more uncertain than that of the first one. Taken as a whole, the test must therefore be considered to verify our assumptions that only mononuclear complexes are formed and that the values of the previous uranyl measurements may be used even in the present medium.

SUMMARY

The complexities of the chloride, bromide and thiocyanate systems of uranium (IV) are determined from measurements of the UO_2^{2+}/U^{4+} redox couple utilizing the known values of complexity of the corresponding uranyl systems. The measurements are performed at 20° C in a perchlorate medium of the ionic strength 1 C.

A constant acidity is maintained which is chosen so high ($[H^+] = 600$ mC) that no hydrolysis exists. In order to bring about the necessary acceleration of the potential adjustment, an addition of indigotetrasulfonate is found suitable. The conditions necessary for a proper use of such mediators are discussed.

Only mononuclear complexes seem to exist in the systems investigated. For the chloride and bromide systems only the first complex can be certainly proved. The constants found are 2 C^{-1} and 1.5 C^{-1} respectively. In the thiocyanate system, the first two complexes are certainly proved and possibly the third one also exists. The following constants are computed $\gamma_1 = 31\ C^{-1}$, $\gamma_2 = 90\ C^{-2}$ and $\gamma_3 \approx 150\ C^{-3}$.

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