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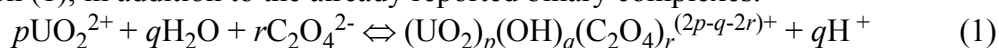
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ON THE HYDROLYSIS OF THE DIOXOURANIUM(VI) ION IN OXALATE SOLUTIONS

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Summary - The complex formation between the dioxouranium (VI) and the oxalate ions has been investigated by measuring the potential of a glass electrode, at 25.00 °C, in 1 and 3 M NaClO₄, at lower acidities than 10^{-4.5} M, in order to favour the formation of (mixed) ternary species. The upper limits of concentration of all the analytical parameters have been imposed by the modest solubility of Na₂C₂O₄ in the ionic media. The experimental measurements at different ionic strengths have been treated by means of the computerised least square programme LETAGROP - ETITR¹. Ternary complexes of general composition (*p*, *q*, *r*) are formed according to reaction (1), in addition to the already reported binary complexes.



The stoichiometric compositions of the ternary species are (1, 1, 1), (2, 4, 2), (2, 2, 4). Their formation constants, expressed in molality, obtained in the two ionic media, are listed below.

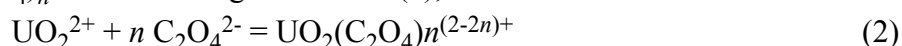
<i>I</i> (m)	log *β _{1,1,1}	log *β _{2,2,4}	log *β _{2,4,2}
3.503	0.81 ± 0.08	11.80 ± 0.05	
1.051	1.39 ± 0.05	10.98 ± 0.11	-8.32 ± 0.11
0 (SIT ²)	2.76 ± 0.10	8.02 ± 0.12	

For reasons discussed in the present work in the last column only the value of the constant in 1 M ionic medium is reported for the species (2, 4, 2). Additional evidence on the stoichiometric composition of the species formed is afforded by the mass-spectrometric measurements, collected in solutions of known composition.

INTRODUCTION

Uranium is a strategic element both for peaceful and war uses. Therefore the abundance of the literature, that has so far been produced, to enlighten the chemical behaviour of its various oxidation (°), Corresponding author; fax: (++39)-081-674379 Tel.: (++39)-081-674380; e-mail: ferri@chemistry.unina.it

states, shall not surprise. In addition, its low radioactivity makes of it a very valid chemical analogue for many actinides characterised by high radioactivity, in the same oxidation state. In fact many of the reactions of uranium(VI, V, IV) are similar to those exhibited by the other actinides in the same oxidation state. Our interest on the chemistry of uranium is partly motivated by the applied aspects and partly by the need of gaining fundamental chemical knowledge on the interactions of uranium (and indirectly other actinides) with the ligands, naturally present in the superficial, as well as in the underground waters. Numerous laboratories, the world over, have since long been engaged to build up a Thermodynamic Data Base (TDB), on which to construct a mathematical model of release and migration of radionuclides, from permanent repositories to the biosphere. Our laboratory has devoted great part of its activity to this issue, for more than two decades. Particular attention has been devoted to the equilibrium reactions between the uranyl (VI) ion and naturally occurring ligands, because of their great importance in the speciation of ground waters. Several studies^{3,4} to interpret the interactions of the carbonate ion and other inorganic ligands, with uranium, in the oxidation states +6, +5, +4, in a large interval of acidity ($3 < pH < 12$), have been carried out. Recently our interest has focused on the oxalic acid and its derivatives, because they are frequently found in natural waters, mainly supplied by the decomposition of vegetal matter which produces fulvic and humic acids, that further decompose into smaller molecules: among them the simplest carboxylic acids. Our first contribution to the binary complex formation between uranyl and oxalate is reported elsewhere^{5,6}. We found evidence, at $pH < 2.5$, of the formation of three mononuclear species $UO_2(C_2O_4)_n^{(2-n)+}$ according to reaction (2),



where $n = 1, 2, 3$, with the following formation constants (valid at $I = 0$): $\log \beta_1^\circ = 7.38 \pm 0.07$, $\log \beta_2^\circ = 11.72 \pm 0.10$, $\log \beta_3^\circ = 12.8 \pm 0.1$. On the other hand the complex formation between uranyl and oxalate ions has been thoroughly studied by Havel⁷ in 1969, by using a spectrophotometric method, in 1 M $NaClO_4$ as the ionic medium. The results reported in our two papers^{5,6} are in excellent agreement, as far as the protolysis of $C_2O_4^{2-}$, and the formation constants of the first two complexes $UO_2(C_2O_4)^0$ and $UO_2(C_2O_4)_2^{2-}$ are considered, whereas Havel's third species $UO_2(C_2O_4)_3^{4-}$ exhibits a three orders of magnitude smaller formation constant than ours. The criticism that followed about this discrepancy, was mostly based on the outcomes of X-ray measurements on single crystals, of solid salts which showed that the third oxalate ion binds, on the equatorial plane of UO_2^{2+} "end-on" (see ref. 8, *p.*103-105) because there does not seem to be room for three equivalent oxalate ions. If this geometry also applied in solution, then we ought to expect a much smaller formation constant for the third complex, as it appeared to be the case in Havel's study⁷. However Havel and co-workers⁹ have recently carried out, in 3 M $NaClO_4$, a more extensive spectrophotometric study of this system. Their third constant of formation increases from 11 to 13.8. On the other hand further measurements carried out in our laboratory (this work) have shown that the formation constant of the third uranyl complex decreases from 15.2 to 13.4, in 3 M $NaClO_4$, and compares now satisfactorily with the one re-determined by Havel et al.⁹. We believe that the determination of the third constant is complicated by the low solubility of $Na_2C_2O_4$ in $NaClO_4$, particularly at the 3 M level. Thus high concentration ratios of oxalate over uranyl, which would favour the formation of the (1,3) species, are not attainable. A more detailed history of the studies on the complex formation between uranyl and oxalate ion may be found in the article by Havel et al.⁹. Eventually in relation to the claimed presence of two di-nuclear complexes, namely (2,3) and (2,5), suggested by Havel et al.⁹, we have found no evidence of their formation, although we have covered wider concentration ranges. In the present work, we have intended to investigate

the possibility of the formation of ternary complexes $(\text{UO}_2)_p(\text{OH})_q(\text{C}_2\text{O}_4)_r^{(2p-q-2r)+}$, indicated for brevity as (p, q, r) , in the range $4.5 < \text{pH} < 8.5$.

LIST OF SYMBOLS

All the concentrations are expressed as mol/dm^3 , molarity; molal units, $\text{mol/KgH}_2\text{O}$, are only used when applying the SIT².

$\beta_{p, q, r}$ = equilibrium constant of the reaction (1), valid in the ionic medium;

$h = [\text{H}_3\text{O}^+] =$ free proton concentration;

$b = [\text{UO}_2^{2+}] =$ free dioxouranium (VI) concentration;

$a = [\text{C}_2\text{O}_4^{2-}] =$ concentration of the free oxalate ion;

$c_{p, q, r} = \beta_{p, q, r} b^p h^q a^r =$ concentration of the (p, q, r) complex;

$H = h - [\text{OH}^-] - \sum \sum \sum q c_{p, q, r} =$ analytical protons excess with respect to the zero level represented by H_2O , $\text{C}_2\text{O}_4^{2-}$, UO_2^{2+} ;

$B = [\text{U(VI)}] =$ analytical (total) concentration of U(VI);

$A = [\text{C(III)}] =$ analytical (total) concentration of oxalate;

$Z =$ average number of OH^- bound per UO_2^{2+} ;

$D = 0.51 I^{1/2} / (1 + 1.5 I^{1/2}) =$ Debye's term in the SIT²;

$I = \frac{1}{2} \sum z_i^2 m_i =$ ionic strength, $z_i =$ charge of the ion i and $m_i =$ its molal (weight molarity) concentration;

$\gamma_i =$ activity coefficient of the ion i , in molal units;

$\alpha(i, k) =$ interaction coefficient between species i and k ;

$\log \gamma_i = -z_i^2 D + \sum \alpha(i, k) m_k$ (SIT equation).

EXPERIMENTAL

Reagents and analysis

The stock solutions of $\text{UO}_2(\text{ClO}_4)_2$ were prepared oxidising U_3O_8 by means of HIO_3 in a slight excess of HClO_4 . The preparation and the analysis are described in ref. 10. U_3O_8 was obtained by igniting $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Merck *p.a.* quality) for 24 hours, at 850°C . HIO_3 *p.a.* from Merck was used as such, without further purification.

HClO_4 stock solutions were prepared from the 65% RPE Carlo Erba product and titrated by KHCO_3 , using a mixed methyl red - bromocresol green indicator, with a reproducibility of 0.1%. NaClO_4 stock solutions were synthesised from HClO_4 and Na_2CO_3 (Carlo Erba RPE) as described elsewhere¹¹. They were analysed upon displacing H_2O at 120°C from NaClO_4 and weighing the dry sample until constancy. The acid content was determined by a potentiometric-coulometric titration.

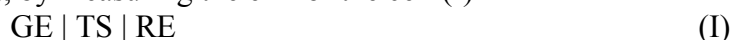
Stock solutions of $\text{Na}_2\text{C}_2\text{O}_4$ were prepared from $\text{Na}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (Carlo Erba RPE) and were periodically standardised by KMnO_4 previously analysed by means of stoichiometric $\text{Na}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$.

Equipment

The Ag,AgCl electrodes were prepared according to Brown¹². The glass membrane electrodes, as well as the automatic burettes, were Metrohm products. The measurements were carried out into an air thermostat, developed in our laboratory, large enough to accommodate two automatic burettes, in addition to the reaction cell. The temperature in the thermostat was maintained constant to within $\pm 0.02^\circ\text{C}$. The experimental data were collected by means of an automatic data acquisition system based on Hewlett and Packard (HP) instrumentation. The MS spectra were registered on a single quadrupole ZQ Micromass (Waters) electrospray mass spectrometer. The solutions were introduced into the ion source, at a flow rate of $30 \mu\text{l min}^{-1}$, by means of a pump acting on the piston of a syringe. A nitrogen flow of $260 \text{ dm}^3 \text{ h}^{-1}$ was applied. The spectra were collected in negative ion mode, at 5 s scan^{-1} , over a range from 30 to 2000 m/z . The useful part of the spectrum interval ranged from 250 to 650 m/z as shown in Figs. 2-4. The settings were as follows: capillary at 3.0 kV, cone 20 V, source temperature 120°C .

METHOD AND RESULTS

The formation of the ternary species between UO_2^{2+} and the ligands OH^- and $\text{C}_2\text{O}_4^{2-}$ has been studied at $25.00 \pm 0.02^\circ\text{C}$, in a thermostatted air box, in the presence of NaClO_4 as ionic medium, at two concentrations, 1 and 3 (molar units), by measuring the emf of the cell (I)



in which GE indicates a glass membrane electrode reversible to protons; $\text{RE} = 1 \text{ M NaClO}_4 / 0.010 \text{ M Ag}^+$, $(1 - 0.010) \text{ M Na}^+$, $1 \text{ M ClO}_4^- / \text{AgCl, Ag}$ is an external reference electrode, connected to TS through a salt bridge; TS = test solution of various composition given in the following. For simplicity we have only treated in detail the experimental data collected in 3 M NaClO_4 . The data obtained in 1 M differ from those in 3 M NaClO_4 only for the titration method: coulometric, in 3 M, and volumetric in 1 M. The interpretation technique is identical. The experiments were performed in three steps:

Step I): Determination of E^0 , the glass electrode constant.

A weighed volume $V_0 \text{ cm}^3$ of a test solution, TS, of initial composition $\text{TS}_0 = H_0 \text{ M H}^+$, $B \text{ M UO}_2^{2+}$, $(3.000 - H_0 - 2B) \text{ M Na}^+$, 3.000 M ClO_4^- , in which $0 \leq B \leq 0.01 \text{ M}$ and $H_0 > 0.001 \text{ M}$, is introduced into the measuring vessel. Possible traces of CO_2 , which would favour the formation of carbonate complexes, are displaced by a flow of pure O_2 , preconditioned at the proper vapour pressure, by bubbling through washing bottles containing the same ionic medium as the test solution. Oxygen is used in order to avoid the cathodic reduction of U(VI) to U(IV) which is thermodynamically favoured but kinetically slow. Then H^+ in TS_0 is stepwise reduced at the Pt cathode of circuit (II) until the incipient precipitation of uranyl hydroxides occurs.



In the circuit (II) $\text{AE} = 3.000 \text{ M NaClO}_4 / 0.100 \text{ M Hg}_2^{2+}$, 2.800 M Na^+ , $3.000 \text{ M ClO}_4^- / \text{Hg(Pt)}$ is an external auxiliary electrode, connected to TS through a salt bridge. After each delivery of current of intensity $i(\text{A})$, for a time $t(\text{s})$, the emf, $E(\text{mV})$, of cell (I) is measured until constancy. The Nernst potential of the cell (I), E , can be written as in eqn. (3)

$$E = E^0 + 59.16 \log h \quad (3)$$

where E^0 is the glass electrode constant, h represents the free proton concentration at equilibrium. In eqn. (3) the liquid junction potential¹⁴, $E_j = -16.8 h$, due to the replacement of Na^+ with H^+ , as well as the term accounting for the activity factor changes, can be neglected, because the composition of TS does not differ appreciably from that of the ionic medium. According to Faraday's law, the number of micromoles of reduced H^+ ions, μ , is numerically equal to the microfaradays generated by the circuit (II), eqn. (4)

$$\mu = i * t / 0.096487 \quad (4)$$

Since the hydrolysis of UO_2^{2+} is repressed at acidities, h , greater than 10^{-3} M, the concentration of free H^+ ions in the solution is equal to H , which is the analytical excess of H^+ ions, in the course of the titration, and is given by the relationship (5),

$$h = H = (n_0 - \mu) / (V_0 * 1000) \quad (5)$$

n_0 represents the initial number of micromoles of protons in the volume, V_0 , of TS_0 . Introducing eqn. (5) into eqn. (3) we obtain eqn (6).

$$E = E^0 + 59.16 \log ((n_0 - \mu) / (V_0 * 1000)) \quad (6)$$

Eqn (6) can advantageously be transformed into a linear function, *i.e.* a Gran¹³ plot, which provides the value of n_0 , as well as E_0 , that are indispensable for the next steps.

Step II): Hydrolysis of the UO_2^{2+} ion.

The hydrolysis of UO_2^{2+} has been studied in various ionic media, as reported in the pertinent literature^{3,4,15} by using several investigation methods. We have however repeated the measurements in order to improve the values of the formation constant of the mononuclear species UO_2OH^+ , which is not well known and is not an entirely negligible species in our dilute ($B < 0.01$ M) solutions. The solution resulting from the step I has composition $\text{TS} = \text{TS}_1 = H_1 \text{ M } \text{H}^+$, $B \text{ M } \text{UO}_2^{2+}$, $(3.000 - H_1 - 2B) \text{ M } \text{Na}^+$, $3.000 \text{ M } \text{ClO}_4^-$ and is used to carefully evaluate the formation constants of the binary hydrolysed species. The investigation has been undertaken by using the same coulometric procedure illustrated above, at four concentrations of the ionic medium (0.5 M, 1 M, 2 M, 3 M). The hydrolysis initiates at $-\log h > 3$ if B is lower than 0.01M. Experimentally the hydrolysis is carried out, by stepwise decreasing the acidity of the solution TS_1 , (while maintaining B constant) by the same procedure as the one illustrated in the step I. (*) The sets of data $E(\mu)_B$, resulting for each ionic strength, are interpreted both by the computerised least square programme LETAGROP-ETITR¹ and by graphical methods¹⁶. The results are resumed in Table 1, where the values of equilibrium constants, extrapolated at infinite dilution, by SIT², are given (in the last row). Our values of the equilibrium constants, as well as the stoichiometric composition of the complexes formed, agree excellently with those recommended in the compilation, supported by NEA-OECD^{3,4}.

(*)Some titrations have been carried out by replacing the cells (I) and (II) with the junctionless cells (III) and (IV) :



where $\text{TS} = B \text{ M } \text{UO}_2^{2+}$, $H \text{ M } \text{H}^+$, $C \text{ M } \text{Ag}^+$, $D \text{ M } \text{Pb}^{2+}$, $(3.000 - 2B - H - C - 2D) \text{ M } \text{Na}^+$, $3.000 \text{ M } \text{ClO}_4^-$. The cell (IV) is particularly advantageous since Pb^{2+} and Ag^+ hydrolyse at lower acidities than UO_2^{2+} . The data collected by the cells (III) and (IV) fully confirm the values of the hydrolysis constants obtained by cells (I) and (II), suggesting that no serious error can occur in our measurements if we evaluate the liquid junction potential¹⁴ by the relation $E_j = -16.8 h$.

TABLE 1 - The hydrolysis constants, $^*\beta_{p,q}$, of the species (1, 1), (2, 2) and (3, 5) obtained at four ionic media both in molarity (M) and molality (m). In the last row the values extrapolated to $I = 0$, by the SIT², are reported.

NaClO ₄ (M)	$\log M^*\beta_{1,1}$	$\log M^*\beta_{2,2}$	$\log M^*\beta_{3,5}$	NaClO ₄ (m)	$\log m^*\beta_{1,1}$	$\log m^*\beta_{2,2}$	$\log m^*\beta_{3,5}$
0.500	-4.60±0.02	-5.86±0.05	-15.50±0.07	0.513	-4.59±0.02	-5.85±0.05	-15.47±0.07
1.000	-4.73±0.03	-5.90±0.02	-15.79±0.02	1.051	-4.71±0.03	-5.88±0.02	-15.72±0.01
2.000	-4.91±0.11	-5.98±0.03	-16.14±0.02	2.212	-4.87±0.11	-5.94±0.03	-16.01±0.02
3.000	-5.06±0.17	-6.04±0.04	-16.11±0.02	3.503	-4.99±0.17	-5.97±0.04	-15.91±0.02
				0	-4.2±0.10	-5.49±0.06	-14.5 ± 0.20

Step III): Study of the ternary system UO_2^{2+} - OH^- - $C_2O_4^{2-}$

The V_0 cm³ of the solution resulting from step II) have composition $TS = TS_2 = H_2$ M H^+ , B M UO_2^{2+} , $(3.000 - H_2 - 2B)$ M Na^+ , 3.000 M ClO_4^- where $0 \leq B \leq 0.01$ M and $H < 0.001$ M. The third step initiates by the addition of a weighed volume of solution $T_1 = H_3$ M H^+ , A M $C_2O_4^{2-}$, $(3.000 - H_3 + 2A)$ M Na^+ , 3.000 M ClO_4^- , to obtain TS_3 , having a pre-established value of the ratio A/B . $TS_3 = H_4$ M H^+ , B_3 M UO_2^{2+} , A_3 M $(C_2O_4^{2-})$, $(3.000 - H_4 + 2A_3 - 2B_3)$ M Na^+ , 3.000 M ClO_4^- . As we anticipated above, the upper concentration limit of A is determined by the low solubility of oxalate in the ionic media (in 3 M $NaClO_4$ it does not exceed the 0.015 M level). Consequently the concentration of uranium (VI) was kept below 0.01 M. The acidity level of the resulting TS_3 solution is stepwise decreased, coulometrically, by circuit (II), until the precipitation of a yellow solid¹⁷ takes place. After each removal of μ micromoles of H^+ , the potential E of cell (I) is measured. The experimental data $E(H, h)_{A/B}$, obtained for different values of the ratio A/B , in 1 and 3 M $NaClO_4$, have been recalculated as the formation function $Z(-\log h)_{A/B} = (h - H)B^{-1}$ (see Table 2 and Fig.1). They have been interpreted, in terms of the ternary complexes (1, 1, 1), (2, 4, 2) and (2, 2, 4), by LETAGROP-ETITR¹, minimising the function $U = \Sigma(H_{calc} - H_{exp})^2$. No systematic deviation was observed assuming the stoichiometric compositions and the formation constants reported in Table 3. They have been used to construct the model curves¹⁶ (solid lines) in Fig.1. In 1 M $NaClO_4$ out of 173 points collected, 96 exhibit positive values of $\Delta H = (H_{calc} - H_{exp})$ and 77 negative. In 3 M $NaClO_4$ 212 points were analysed of which 109 show positive ΔH and 94 negative. The determination of the values of the formation constants of the (1, 1, 1) and (2, 4, 2) has been rather problematic because the former rarely attains important concentration levels, while the latter is principally formed only at 1 M ionic strength, where higher $-\log h$ values may be reached, before precipitation occurs. Distribution diagrams, valid in 1 M $NaClO_4$, are reported in Fig. 2.

$I = 1 \text{ M NaClO}_4$

$A = 0.0050 \text{ M}; B = 0.0050 \text{ M}$

0.225(4.233); 0.578(4.729); 0.748 (4.936);

$A = 0.0050 \text{ M}; B = 0.0050 \text{ M}$

0.204 (4.192); 0.375(4.412); 0.510(4.594); 0.642(4.821); 0.691 (4.918); 0.722(4.975);

$A = 0.024 \text{ M}; B = 0.0050 \text{ M}$

0.061(6.126); 0.083(6.202); 0.104(6.267); 0.126(6.326); 0.148(6.38); 0.169(6.434); 0.191(6.482); 0.213(6.502); 0.235(6.544); 0.256 (6.591); 0.278(6.628);

$A = 0.025 \text{ M}; B = 0.0050 \text{ M}$

0.001(5.908); 0.022(6.006); 0.043(6.085); 0.063(6.16); 0.084(6.224); 0.105(6.289); 0.125(6.347); 0.146(6.398); 0.167(6.453); 0.188 (6.501);

$A = 0.025 \text{ M}; B = 0.0050 \text{ M}$

0.057(6.214); 0.105(6.334); 0.172(6.453); 0.202(6.499); 0.238(6.562); 0.307(6.663); 0.363(6.741); 0.416(6.819); 0.454(6.856); 0.554 (7.013); 0.656(7.15); 0.763(7.284); 0.853(7.39); 0.949(7.506); 1.043(7.628);

$A = 0.025 \text{ M}; B = 0.0052 \text{ M}$

0.108 (6.445); 0.309 (6.711); 0.424 (6.86); 0.474 (6.93); 0.52 (6.993); 0.583 (7.068); 0.621 (7.11); 0.683 (7.191); 0.742 (7.267); 0.881 (7.42); 1.043 (7.606); 1.088 (7.652); 1.139 (7.686);

$A = 0.025 \text{ M}; B = 0.0051 \text{ M}$

0.011 (6.008); 0.054 (6.14); 0.108 (6.226); 0.203 (6.426); 0.297 (6.637); 0.352 (6.706); 0.407 (6.767); 0.479 (6.871); 0.532 (6.972); 0.567 (7.018); 0.602 (7.086); 0.654 (7.139); 0.74 (7.28); 0.799 (7.357); 0.856 (7.428); 0.986 (7.593);

$A = 0.050 \text{ M}; B = 0.0050 \text{ M}$

0.068 (6.62); 0.281 (6.987); 0.37 (7.094); 0.541 (7.357);

$I = 3 \text{ M NaClO}_4$

$A = 0.0087 \text{ M}, B = 0.0027 \text{ M};$

-0.133(4.722); -0.114(4.774); -0.096(4.840); -0.078(4.911); -0.059(4.991); -0.041(5.084).

$A = 0.016 \text{ M}, B = 0.0051 \text{ M};$

-0.462 (3.783); -0.426 (3.871); -0.394 (3.947); -0.359 (4.022); -0.323 (4.099); -0.287 (4.191); -0.251 (4.281); -0.214 (4.382); -0.177 (4.499); -0.14 (4.638); -0.103 (4.815); -0.065 (5.041); -0.027 (5.318); 0.011 (5.588); 0.05 (5.797); 0.206 (6.304); 0.245 (6.391); 0.284 (6.473); 0.323 (6.548); 0.362 (6.621); 0.402 (6.688); 0.441 (6.753); 0.48 (6.815); 0.519 (6.876); 0.558 (6.933);

$A = 0.0050 \text{ M}, B = 0.0050 \text{ M};$

0.048(3.317); 0.044(3.604); 0.059(3.928); 0.091(4.131); 0.129(4.258); 0.168(4.356); 0.208(4.439); 0.248(4.516); 0.288(4.591); 0.328(4.664); 0.369(4.740); 0.410(4.817); 0.451(4.897); 0.491(4.980); 0.532(5.067); 0.573(5.156); 0.614(5.240); 0.655(5.322);

$A = 0.0050 \text{ M}, B = 0.0050 \text{ M};$

0.031(2.713); 0.027(2.785); 0.024(2.872); 0.020(2.981); 0.017(3.124); 0.016(3.332); 0.021(3.664); 0.052(4.026); 0.100(4.232); 0.152(4.362); 0.206(4.470); 0.259(4.568); 0.314(4.665); 0.368(4.763); 0.422(4.863); 0.477(4.969); 0.532(5.081); 0.586(5.199).

$A = 0.0050 \text{ M}, B = 0.0144 \text{ M};$

0.013(2.749); 0.010(2.833); 0.010(2.921); 0.013(3.018); 0.018(3.121); 0.026(3.215); 0.038(3.299); 0.049(3.371); 0.067(3.432); 0.083(3.485); 0.099(3.533); 0.116(3.574); 0.134(3.610); 0.152(3.644); 0.169(3.675); 0.187(3.705); 0.205(3.732); 0.224(3.757); 0.242(3.782); 0.261(3.794); 0.279(3.827); 0.297(3.849); 0.316(3.870); 0.334(3.889); 0.353(3.909); 0.371(3.928); 0.390(3.946); 0.409(3.965);

$A = 0.0148 \text{ M}, B = 0.0096 \text{ M};$

0.006(3.232); 0.006(3.346); 0.008(3.471); 0.012(3.627); 0.016(3.823); 0.023(4.047); 0.045(4.403); 0.058(4.519); 0.071(4.608); 0.084(4.684); 0.097(4.751); 0.111(4.813); 0.124(4.871); 0.138(4.926); 0.151(4.980); 0.165(5.033); 0.178(5.085); 0.199(5.163); 0.219(5.241); 0.239(5.317); 0.260(5.396); 0.280(5.473); 0.301(5.550); 0.321(5.623); 0.342(5.710); 0.362(5.776); 0.383(5.839); 0.41(5.924).

$A = 0.0089 \text{ M}, B = 0.0052 \text{ M};$

-0.097(2.267); -0.090(2.326); -0.080(2.393); -0.078(2.432); -0.072(2.473); -0.067(2.518); -0.062(2.569); -0.059(2.601); -0.056(2.634); -0.051(2.669); -0.049(2.710); -0.039(2.797); -0.032(2.846); -0.024(2.922); -0.014(3.01); -0.005(3.124); 0.006(3.267); 0.013(3.359); 0.026(3.628); 0.035(3.836); 0.046(4.159); 0.063(4.636); 0.086(5.020); 0.112(5.269); 0.138(5.444); 0.164(5.583); 0.190(5.702); 0.216(5.802); 0.242(5.889); 0.268(5.971); 0.294(6.044); 0.311(6.088); 0.329(6.129); 0.346(6.171); 0.364(6.209); 0.381(6.243); 0.398(6.279); 0.416(6.313); 0.433(6.344); 0.445(6.376); 0.463(6.404); 0.485(6.431); 0.503(6.461).

FIG.1 - Ternary complex formation in the system UO_2^{2+} - OH^- - $\text{C}_2\text{O}_4^{2-}$. The symbols represent the experimental formation function $Z(-\log h)_{A/B}$. The solid curves represent the model of complexation proposed and have been calculated by using the values of the equilibrium constants, valid in 1M NaClO_4 (a) and 3 M NaClO_4 (b), reported in Table 3. Concerning the data with $A/B = 0$ (hydrolysis of UO_2^{2+}) only every second point has been reported not to burden the figure excessively.

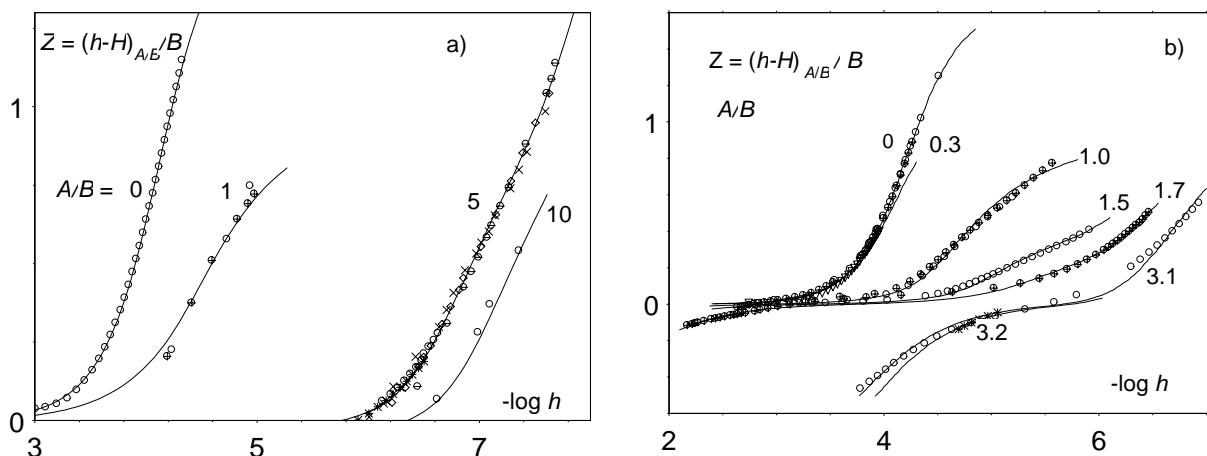
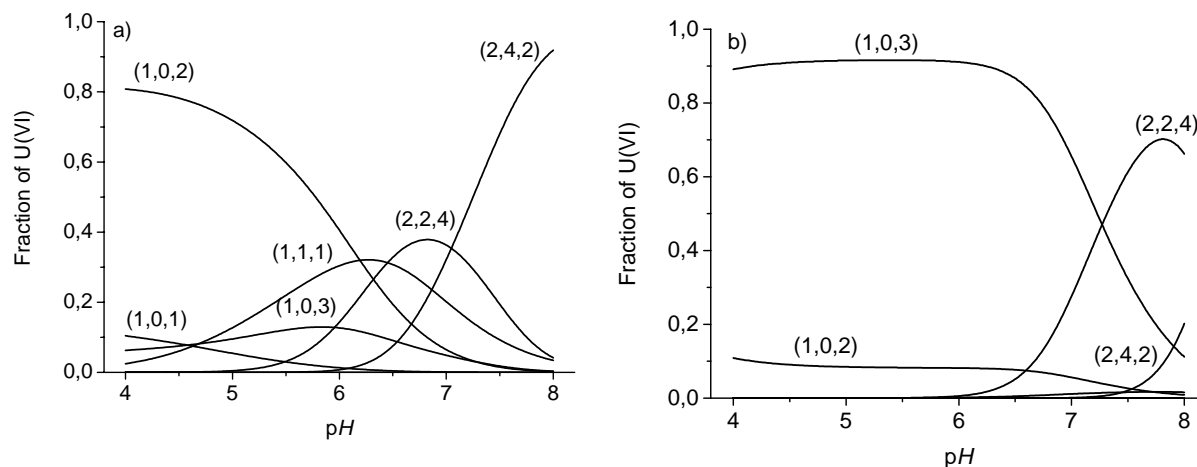


TABLE 3 – In the first column a survey of the main reactions occurring in the UO_2^{2+} , OH^- , $\text{C}_2\text{O}_4^{2-}$ system is presented. In the second (1 M NaClO_4) and the third (3 M NaClO_4) the logarithms of the values of the constants are reported followed, by three times the standard deviation.

Reaction	Ionic medium		Ref.
	1 M NaClO_4	3 M NaClO_4	
$\text{H}^+ + \text{C}_2\text{O}_4^{2-} = \text{HC}_2\text{O}_4^-$	3.57 ± 0.02	3.80 ± 0.05	5
$2\text{H}^+ + \text{C}_2\text{O}_4^{2-} = \text{H}_2\text{C}_2\text{O}_4$	4.57 ± 0.02	4.94 ± 0.05	5
$\text{UO}_2^{2+} + \text{H}_2\text{O} = \text{UO}_2\text{OH}^+ + \text{H}^+$	-4.73 ± 0.03	-5.06 ± 0.17	p. w.
$\text{UO}_2^{2+} + 2 \text{H}_2\text{O} = (\text{UO}_2)_2(\text{OH})_2^{2+} + 2 \text{H}^+$	-5.90 ± 0.02	-6.04 ± 0.04	p. w.
$3 \text{UO}_2^{2+} + 5 \text{H}_2\text{O} = (\text{UO}_2)_3(\text{OH})_5^+ + 5 \text{H}^+$	-15.79 ± 0.02	-16.11 ± 0.02	p. w.
$\text{UO}_2^{2+} + \text{C}_2\text{O}_4^{2-} = \text{UO}_2\text{C}_2\text{O}_4$	6.02 ± 0.03	6.39 ± 0.01	5
$\text{UO}_2^{2+} + 2 \text{C}_2\text{O}_4^{2-} = \text{UO}_2(\text{C}_2\text{O}_4)_2^{2-}$	10.55 ± 0.06	11.52 ± 0.02	5
$\text{UO}_2^{2+} + 3 \text{C}_2\text{O}_4^{2-} = \text{UO}_2(\text{C}_2\text{O}_4)_3^{4-}$	13.02 ± 0.09	$13.4 \pm 0.10^{**}$	5
$\text{UO}_2^{2+} + \text{H}_2\text{O} + \text{C}_2\text{O}_4^{2-} = (\text{UO}_2)(\text{OH})(\text{C}_2\text{O}_4)^- + \text{H}^+$	1.39 ± 0.05	0.81 ± 0.08	p. w.
$2 \text{UO}_2^{2+} + 2 \text{H}_2\text{O} + 4 \text{C}_2\text{O}_4^{2-} = (\text{UO}_2)_2(\text{OH})_2(\text{C}_2\text{O}_4)_4^{6-} + 2 \text{H}^+$	11.05 ± 0.11	12.00 ± 0.05	p. w.
$2 \text{UO}_2^{2+} + 4 \text{H}_2\text{O} + 2 \text{C}_2\text{O}_4^{2-} = (\text{UO}_2)_2(\text{OH})_4(\text{C}_2\text{O}_4)_2^{4-} + 4 \text{H}^+$	-8.34 ± 0.11		p. w.
p. w.: present work			
**recalculated in this work			

FIG.2 - The distribution diagrams, valid in 1 M NaClO₄: a) $B = 0.005$ M and $A = 0.010$ M; b) $B = 0.005$ M and $A = 0.050$ M.



EXTRAPOLATION TO ZERO IONIC STRENGTH BY SIT²

The equilibrium constants accurately determined in the ionic media have been recalculated on the thermodynamic scale (infinite dilution). To this scope we have chosen the SIT², which involves fewer parameters than, for instance, the Pitzer equation and gives comparable results. The general relations, written for both the hydrolysis of UO_2^{2+} (eq. 7) and for the mixed species (eq. 8), are immediately obtained from the SIT equation given in the paragraph LIST OF SYMBOLS:

$$F_{p,q} = \log^* \beta_{p,q} - q \log a_w + D[-(2p - q)^2 - q + 4p] = \log^* \beta_{p,q}^\circ - \Delta \varepsilon(p, q) m_{\text{ClO}_4} \quad (7)$$

$$F_{p,q,r} = \log^* \beta_{p,q,r} - q \log a_w - D \{ [2(p - r) - q]^2 - q + 4(p + r) \} = \log^* \beta_{p,q,r}^\circ - \Delta \varepsilon(p, q, r) m_{\text{ClO}_4} \quad (8)$$

By reporting $F_{p,q}$ and $F_{p,q,r}$ vs. $m_{\text{ClO}_4^-}$ the $\log^* \beta_{p,q}^\circ$ and $\log^* \beta_{p,q,r}^\circ$ are respectively determined as the intercepts. $\Delta \varepsilon(p, q)$ and $\Delta \varepsilon(p, q, r)$ are contextually furnished as the slopes of the straight lines and are defined as follows:

$$\Delta \varepsilon(p, q) = \varepsilon((p, q), \text{Na}^+ \text{ or } \text{ClO}_4^-) + q \varepsilon(\text{H}^+, \text{ClO}_4^-) - p \varepsilon(\text{UO}_2^{2+}, \text{ClO}_4^-).$$

$$\Delta \varepsilon(p, q, r) = \varepsilon((p, q, r), \text{Na}^+ \text{ or } \text{ClO}_4^-) + q \varepsilon(\text{H}^+, \text{ClO}_4^-) - p \varepsilon(\text{UO}_2^{2+}, \text{ClO}_4^-) - r \varepsilon(\text{C}_2\text{O}_4^{2-}, \text{Na}^+).$$

The ε values, expressed in Kg mol^{-1} , used or determined in this work, are listed below together with a number of previously published values (Tab.3 of ref. 5) that have been recalculated.

$\varepsilon(\text{H}^+, \text{ClO}_4^-) = 0.14 \text{ m}^{-1}$; $\varepsilon(\text{UO}_2^{2+}, \text{ClO}_4^-) = 0.46 \text{ m}^{-1}$; $\varepsilon((1, 1), \text{ClO}_4^-) = 0.39 \pm 0.06 \text{ m}^{-1}$; $\varepsilon((2, 2), \text{ClO}_4^-) = 0.60 \pm 0.12 \text{ m}^{-1}$; $\varepsilon((5, 3), \text{ClO}_4^-) = 0.61 \pm 0.17 \text{ m}^{-1}$; $\varepsilon(\text{C}_2\text{O}_4^{2-}, \text{Na}^+) = -0.05 \text{ m}^{-1}$; $\varepsilon(\text{H}^+, \text{C}_2\text{O}_4^{2-}) = 0.12 \text{ m}^{-1}$; $\varepsilon(\text{HC}_2\text{O}_4^-, \text{Na}^+) = -0.05 \text{ m}^{-1}$; $\varepsilon(\text{H}_2\text{C}_2\text{O}_4^0, \text{NaClO}_4) = 0.03 \text{ m}^{-1}$; $\varepsilon((\text{UO}_2)(\text{C}_2\text{O}_4)^0, \text{NaClO}_4) = 0.13 \text{ m}^{-1}$; $\varepsilon(\text{UO}_2(\text{C}_2\text{O}_4)_2^{2-}, \text{Na}^+) = -0.16 \text{ m}^{-1}$; $\varepsilon(\text{UO}_2(\text{C}_2\text{O}_4)_3^{4-}, \text{Na}^+) = 0.20 \text{ m}^{-1}$; $\varepsilon((1, 1, 1), \text{Na}^+) = 0.38 \text{ m}^{-1}$; $\varepsilon((2, 2, 4), \text{Na}^+) = 0.33 \text{ m}^{-1}$.

SPECTROSCOPIC MEASUREMENTS

Our interest in the applications of mass spectroscopy (MS) to inorganic solutions, particularly the solutions characterized by a state of chemical equilibrium, is rather recent. At any rate we have undertaken to perform MS measurements on a solution containing oxalate and uranyl at a

concentration ratio 2 to 1 at $pH=7$, in addition to ClO_4^- and Na^+ ions, at a concentration level not exceeding 0.01 M. Our elementary hypothesis has been based on the assumption that some of the equilibrium species, in the solution at room temperature ($25^\circ C$), could be stable enough to resist the severe experimental conditions of MS, for the time necessary to its instrumental identification. If this were the case, the species would produce signals at the proper m/z ratio. The MS spectra are plotted in Fig. 3 and interpreted in Table 4. The mixed complexes (1, 1, 1), (2, 4, 2) and (2, 2, 4), with charge -1 , -4 and -6 respectively, partially neutralized by the most abundant counter ion, Na^+ , and surrounded by increasing number of water molecules and ClO_4^- ion, can be easily recognised through their m/z ratio. Signals relative to the binary species are also detected. The identification of the most significant peaks has been done, by comparing the spectra of the solution containing uranium to a blank containing $C_2O_4^{2-}$. One may incidentally observe that at m/z values of 331.17 and 367.09 two stoichiometric composition may be ascribed at each one of the two peaks: a case which fortunately does not occur frequently.

FIG. 3 - MS spectra of the system $UO_2^{2+} - OH^- - C_2O_4^{2-}$, recorded in the range $260 < m/z < 700$, in a solution of ratio $A/B = 2$ ($B = 0.01$ M) at $-\log h = 7$. The underlined peaks indicate uranium bearing species. The interpretation of the spectra, in terms of stoichiometric composition, is reported in Table 4.

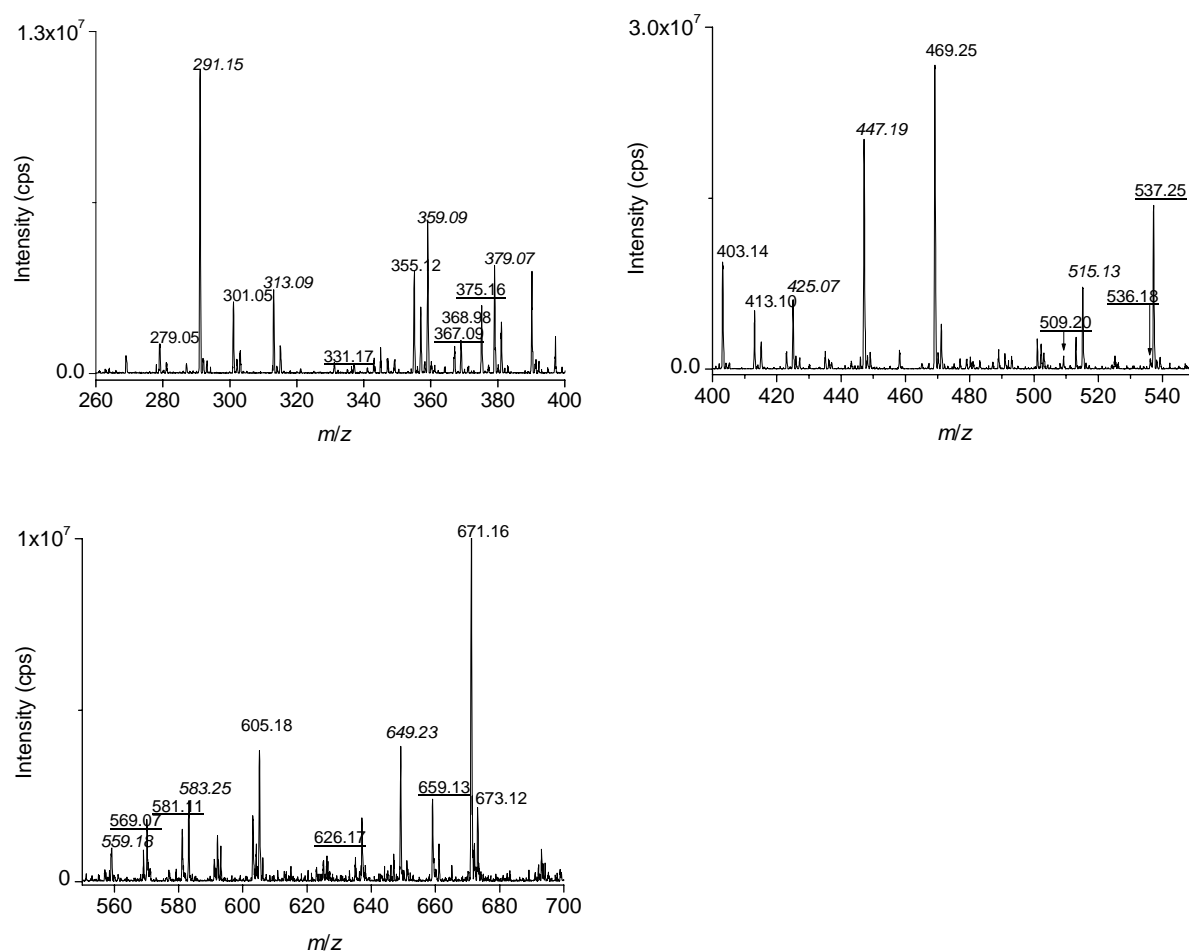


TABLE 4 - Interpretation of MS-spectra. The first column gives the main m/z values observed, which have been interpreted in terms of the composition of the uranyl complexes, listed in the second column. Binary species have also been considered. Several other peaks are observed which may be related to species not bearing uranium and thus not straightforwardly useful for the present investigation.

observed m/z	Assigned stoichiometric composition
375.16	$(\text{UO}_2)(\text{OH})(\text{C}_2\text{O}_4)^-$
569.07	$(\text{UO}_2)(\text{OH})(\text{C}_2\text{O}_4)(\text{Na})(\text{ClO}_4)(\text{H}_2\text{O})_4^-$
537.25	$(\text{UO}_2)(\text{OH})(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_9^-$
659.13	$(\text{UO}_2)(\text{OH})(\text{C}_2\text{O}_4)(\text{Na})(\text{ClO}_4)(\text{H}_2\text{O})_9^-$
331.17	$(\text{UO}_2)_2(\text{OH})_4(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_{30}^{4-}$
367.09	$(\text{UO}_2)_2(\text{OH})_4(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_{38}^{4-}$
509.20	$(\text{UO}_2)_2(\text{OH})_2(\text{C}_2\text{O}_4)_4(\text{Na})_4^{2-}$
536.18	$(\text{UO}_2)_2(\text{OH})_2(\text{C}_2\text{O}_4)_4(\text{Na})_4(\text{H}_2\text{O})_3^{2-}$
581.11	$(\text{UO}_2)_2(\text{OH})_2(\text{C}_2\text{O}_4)_4(\text{Na})_4(\text{H}_2\text{O})_8^{2-}$
626.17	$(\text{UO}_2)_2(\text{OH})_2(\text{C}_2\text{O}_4)_4(\text{Na})_4(\text{H}_2\text{O})_{13}^{2-}$
331.17	$(\text{UO}_2)(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_{12}^{2-}$
349.26	$(\text{UO}_2)(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_{14}^{2-}$
358.27	$(\text{UO}_2)(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_{15}^{2-}$
367.09	$(\text{UO}_2)(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_{16}^{2-}$
469.25	$(\text{UO}_2)(\text{C}_2\text{O}_4)_2(\text{Na})^-$
487.15	$(\text{UO}_2)(\text{C}_2\text{O}_4)_2(\text{Na})(\text{H}_2\text{O})^-$
577.01	$(\text{UO}_2)(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_6^{2-}$
613.19	$(\text{UO}_2)(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_8^{2-}$
603.23	$(\text{UO}_2)(\text{C}_2\text{O}_4)_3(\text{Na})^{3-}$
693.03	$(\text{UO}_2)(\text{C}_2\text{O}_4)_3(\text{Na})_3(\text{H}_2\text{O})_5^-$

DISCUSSION

The system UO_2^{2+} , OH^- , $\text{C}_2\text{O}_4^{2-}$ is definitely laborious to investigate, since it involves the possible coexistence of more than 10 equilibrium species. To simplify the problem, we have divided the pH range into the following segments: from 0 to 2.5 (study of the binary system UO_2^{2+} , $\text{C}_2\text{O}_4^{2-}$)⁵, from 2.5 to 4.5 (study of uranyl hydrolysis, in absence of oxalate) (this work) and from 4.5 to 8.5 (study of ternary species) (this work). This experimental approach has facilitated the determination of the stoichiometric composition of the three ternary complexes found. As to the choice of the experimental techniques, in a complicated and unknown polynuclear system, the determination of the composition can rarely be done using other experimental approaches than the potentiometric one. Other methods (X-ray in sufficiently concentrated solutions, NMR, IR, Fluorescence, etc.) can give very useful information on the structure of the complexes (that is also very important). However, when the stoichiometric composition has to be found, potentiometry is the most powerful

experimental method. Obviously the adoption of as many as possible techniques has to be encouraged, for a more complete characterization of the system investigated. The mass spectrometry (MS) methodology is of paramount importance for investigations in bio and organic chemistry. More recently it has been used in studies of inorganic equilibrium solutions, mostly in mononuclear systems. However we think that this technique is going to become one of the most valid support for Equilibrium Analysis, for the validation of the stoichiometry of polynuclear species, particularly in studies in which large polynuclear species are formed and potentiometry alone cannot distinguish among a number of possible stoichiometric compositions. In these cases MS could produce fundamental evidence on the choice to make. However this approach may only be adopted when a first selection of the possible stoichiometries has been made, on the basis of potentiometric or other equilibrium analysis methods. To tackle this problem by only using the information from MS would hardly be successful. We intend to explore the possibility to extend the application of MS to dubious interpretation of equilibrium data of complicated systems.

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