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Dioxouranium(VI) oxalate complexes†

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The complex formation between dioxouranium(VI) and oxalate ion has been investigated, at 25.00 °C, in 2 and 3 M $NaClO_4$, by measuring the potentials of a glass and of a $Hg_2C_2O_4$–Hg electrode. In the analysed solutions the upper limit of the uranium(VI) concentration did not exceed 0.03 M, the oxalate concentration was imposed by the modest solubility of its sodium salt in the ionic media (about 0.015 M in 3 M $NaClO_4$) and the acidity was kept at levels higher than 0.01 M in order to hinder formation of hydrolysed and possible ternary species. The measurements have been interpreted by assuming the formation of mononuclear complexes only, according to the reaction $UO_2^{2+} + p\, C_2O_4^{2-} \rightleftharpoons UO_2(C_2O_4)_p^{(2-2p)+}$. The equilibrium constants have been extrapolated to infinite dilution by applying the Specific Interaction Theory (SIT) and, in weight molarity (molality) units, are log $^0\beta_1 = 7.38 \pm 0.07$, log $^0\beta_2 = 11.7_2 \pm 0.1$, log $^0\beta_3 = 13.6 \pm 0.2$. Under the same experimental conditions the protolysis constants of oxalic acid and several interaction coefficients, necessary for extrapolation of the results to the thermodynamic scale of activities, through the SIT, have also been determined.

Introduction

Oxalic acid and its salts are not rare in nature. They are even present in edible products, but mainly originate from the complicated and substantially unknown processes of decomposition of vegetal material, which give rise to a multitude of organic compounds. These range from the large humic and fulvic to the simplest mono- and di-carboxylic acids, among which oxalic is one of the most important. Ultimately oxalate ion reaches the deep underground waters and together with other strong ligands, such as hydroxyl, carbonate, fluoride, phosphate, *etc.*, may bind toxic metal ions and transport them to the biosphere. Among these the radio-nuclides from the spent fuel of nuclear power plants, to be disposed of in repositories according to the safety assessed plans of several countries, are certainly the most dangerous.

Oxalic acid is also produced industrially. A number of processes of synthesis have been developed to meet the increasing world demand. It is in fact largely used in industrial preparations for the removal of rust and carbonaceous incrustations, in the household, in dyeing of fabrics in the textile industries, in paper and ink production, in laundries as a stain remover and in many other applications.[2]

Another field in which oxalate ion plays an important role is related to the urinary pathologies determined by kidney stones[3] formation, since calcium oxalate accounts for 90% of the composition of the calculi, whose genesis is to a large extent uncertain. Finally oxalic acid is toxic. The F.D.A.[2] in U.S.A. labels preparations, containing more than 10% of the acid, as a poison that can cause death upon ingestion.

In our opinion this brief account on the origin, uses and domains of oxalic acid and its derivatives amply justifies the development of electrodes capable of measuring accurately the concentration of $C_2O_4^{2-}$, thus allowing the direct study of metal oxalate systems, which have so far been investigated by determining the H^+ (or an auxiliary ion) concentration of oxalate solutions. In a previous paper[4] we reported on a PbC_2O_4(s)–Pb second type electrode which exhibits excellent performance at acidity not lower than 3×10^{-3} M, in reducing solutions compatible with the existence of lead metal. In the present article we describe the construction and demonstrate the Nernstian behaviour of a $Hg_2C_2O_4$(s)–Hg electrode which has been proved to perform reversibly, in oxidising media, at acidity exceeding the 3 M level. This electrode is then used to study the complex formation between UO_2^{2+} and $C_2O_4^{2-}$.

List of symbols

All the concentrations are expressed as molarities M (mol dm^{-3}). A = Analytical (total) concentration of oxalate, $a = [C_2O_4^{2-}]$ = concentration of free oxalate ion, H = analytical excess of protons, $h = [H^+]$ = free proton concentration, $B = [U^{VI}]$ = analytical (total) concentration of uranium in the oxidation state +6 and $b = [UO_2^{2+}]$ = free dioxouranium(VI) (uranyl) concentration. Z = Average number of $C_2O_4^{2-}$ bound per U^{VI}, $Q = H/A$.

$\beta_p = [UO_2(C_2O_4)_p^{(2-2p)+}][UO_2^{2+}]^{-1}[C_2O_4^{2-}]^{-p} = [UO_2(C_2O_4)_p^{(2-2p)+}]b^{-1}a^{-p}$ = equilibrium constant of reaction (1). $K_1 = [HC_2O_4^-][C_2O_4^{2-}]^{-1}\ [H^+]^{-1} = [HC_2O_4^-](ah)^{-1}$ = equilibrium constant of reaction (2). $K_2 = [H_2C_2O_4][HC_2O_4^-]^{-1}\ [H^+]^{-1} = [H_2C_2O_4]([HC_2O_4^-]h)^{-1}$ = equilibrium constant of reaction (3).

$$UO_2^{2+} + pC_2O_4^{2-} \rightleftharpoons [UO_2(C_2O_4)_p]^{(2-2p)-} \qquad (1)$$

$$H^+ + C_2O_4^{2-} \rightleftharpoons HC_2O_4^- \qquad (2)$$

$$H^+ + HC_2O_4^- \rightleftharpoons H_2C_2O_4 \qquad (3)$$

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† Studies on metal oxalate complexes. Part 2.[1]

Electronic supplementary information (ESI) available: a Gran plot of the potentiometric data and experimental data corresponding to Figs. 1–4. See http://www.rsc.org/suppdata/dt/b0/b006544g/

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$D = 0.51I^{\frac{1}{2}}/(1 + 1.5I^{\frac{1}{2}})$ = Debye's term in the Specific Interaction Theory (SIT).[5] $I = \frac{1}{2}\Sigma z_i^2 m_i$ = ionic strength, where z_i = charge of the ion i and m_i = its molal (weight molarity) concentration. γ_i = activity coefficient of ion i, in molal units. $\varepsilon(i,k)$ = interaction coefficient between species i and k. log $\gamma_i = -z_i^2 D + \Sigma\varepsilon(i,k)m_\mathrm{k}$ = SIT equation.

The equilibrium constants K_1, K_2 and β_p are expressed in molar units, whereas ${}^\mathrm{m}K_1$, ${}^\mathrm{m}K_2$ and ${}^\mathrm{m}\beta_p$ represent the corresponding constants on the molal scale of concentrations. Finally ${}^0K_1$, ${}^0K_2$ and ${}^0\beta_p$ indicate the values at zero ionic strength.

Experimental

Reagents and analyses

The stock solutions of $UO_2(ClO_4)_2$ were prepared and analysed as suggested elsewhere,[6] by oxidation of U_3O_8 by means of HIO_3 in a slight excess of $HClO_4$. U_3O_8 was obtained by igniting during 24 hours, at 850 °C, $UO_2(NO_3)_2{\cdot}6H_2O$ of *p.a.* quality, furnished by Merck. 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 analysed by $KHCO_3$, using a mixed methyl red–bromocresol green indicator, with a reproducibility of 0.1%. $NaClO_4$ stock solutions were synthesized from $HClO_4$ and Na_2CO_3 (Carlo Erba RPE) as described elsewhere.[7] They were analysed upon displacing water 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 $Na_2C_2O_4$ prepared from $Na_2C_2O_4{\cdot}2H_2O$ (Carlo Erba RPE) and periodically standardised by $KMnO_4$ which was previously analysed by means of stoichiometric $Na_2C_2O_4{\cdot}2H_2O$. Oxalic acid solutions were prepared by dissolving the Carlo Erba RPE product and analysing them as described for $Na_2C_2O_4$.

Stock solutions of $Hg_2(ClO_4)_2$ were prepared by disproportionation, mixing HgO(s) (Carlo Erba RPE) and Hg 99.999% pure (Fluka) in a slight excess of $HClO_4$. The solution was standardised by a potentiometric-coulometric procedure, measuring the potential of a mercury electrode and by varying the Hg_2^{2+} by reduction at a mercury cathode.

$AuCl_3$ solutions were prepared by simply dissolving the salt in 2 M HCl. PVC [poly(vinyl chloride)] solutions were prepared, shortly before use, by dissolving about 1 g of PVC in 100 cm^3 of THF (tetrahydrofuran).

Equipment

The Ag–AgCl electrodes were prepared according to Brown.[8] 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 burettes, in addition to the reaction cell. The temperature was kept at 25.00 ± 0.02 °C. The experimental data were collected by means of an automatic data acquisition system based on Hewlett and Packard (HP) instrumentation.

In a mercury(I) oxalate $Hg_2C_2O_4$(s)–Hg electrode mercury is usually contained in pools placed on the bottom of the measuring vessel. Such an arrangement however causes a number of problems: the solid usually stratifies on mercury causing a bad electrical contact with the solution; the turbidity does not allow one to look through the solution and to observe whether a precipitate forms within the system investigated; usually a considerable amount of extremely pure, oxide free mercury is needed. We propose here a different construction which essentially consists of coating mercury metal with a layer of $Hg_2C_2O_4$(s). Since this badly adheres to liquid Hg we have adopted the following procedure: a platinum foil or gauze net, having a surface of about 1 cm^2 , is coated by a thin layer of Au, through cathodic reduction from a gold(III) chloride solution (10–20 minutes at 3–5 mA). On the gold layer, following a similar procedure, Hg is deposited from a mercury(I) perchlorate solution, at a current intensity of 0.5–1 mA, usually overnight, to saturate with Hg the resulting solid gold amalgam on which $Hg_2C_2O_4$(s) is finally stratified. For this last step two alternatives have proved convenient: anodic oxidation of (Pt,Au)Hg in an oxalic acid solution affords the best results. Mercury oxalate is precipitated on the gold amalgam at a current intensity of 0.5–1 mA during a couple of hours. Care should be taken to avoid excessive consumption of Hg that would deplete the amalgam and make the behaviour of the electrode unsatisfactory, causing drifting for hours owing to the slow diffusion of Hg through Au. The electrode is finally dipped for a few seconds in a 1% PVC solution in tetrahydrofuran. The second method consists of stratifying freshly prepared $Hg_2C_2O_4$ on the (Pt,Au)Hg electrode. Mercury oxalate is prepared by slow addition of mercury(I) perchlorate (or nitrate) to a solution of $H_2C_2O_4$. The solid is carefully washed and mixed with a few drops of the 1% PVC solution, which helps fix the layer of $Hg_2C_2O_4$ to Hg. After evaporation of the solvent and washing, the electrodes are ready for use, although a couple of days rest improves their behaviour. They tend however to deteriorate, their lifetime seldom exceeding 5 weeks. The performances are comparable, although those prepared by the first method are generally more satisfactory.

Results

Determination of the first protonation constant, K_1, of $C_2O_4^{2-}$

It is worthwhile to state that our project is to study the complex formation between the oxalate ion and uranium in its various oxidation states, much the same as was done for the systems $U^{VI,V,IV}$–carbonate.[9] It seems then important to be able to measure the free oxalate concentration, $[C_2O_4^{2-}]$, in the test solutions.

Prior to undertaking the development of a compact $Hg_2C_2O_4$(s)–Hg electrode, involving no liquid mercury, the Nernstian behaviour of the half cell reaction (4) was demonstrated in a separate, preliminary study[1] in 1 M $NaClO_4$, by using traditional mercury pools, sitting on the bottom of the measuring vessel, with the disadvantages mentioned in the previous section, which made this arrangement (that required manual attention) inadequate for use in our automatic data acquisition systems.

$$Hg_2C_2O_4(s) + 2e^- \longrightarrow 2\,Hg(l) + C_2O_4^{2-} \qquad (4)$$

The electrodes, constructed as described above, were tested in several ways. One (shown in Fig. 1 of ESI) consisted of very precise determinations of the formal standard potential of the couple $Hg_2C_2O_4$(s)–Hg, (defined as E^0 in eqn. (7) below and ESI) as well as the oxalate concentration in solution TS_2. The procedure is practically the same as that illustrated in the second stage.

K_1, the equilibrium constant of reaction (2), was obtained from two sets of independent measurements of the potentials of a glass and of a (Pt,Au)Hg–$Hg_2C_2O_4$(s) electrode, in solutions containing mainly $HC_2O_4^-$ and $C_2O_4^{2-}$. As stated above the upper limit of oxalate concentration did not exceed 0.015 M, furthermore the acidity of the test solutions was generally kept below 0.01 M in order to hinder the formation of appreciable amounts of $H_2C_2O_4$. Consequently the composition of the ionic medium in the course of the titrations remained substantially unchanged. We may thus express the equilibrium constant, K_1, and the Nernst equations in terms of concentrations, since the activity coefficients of all the species are constant.

Two sets of data were obtained in the course of titrations consisting of three stages, here described in detail, since they will be referred to in other sections of this paper.

First stage. A weighed volume $V_0 \approx 50$ cm^3 of a solution TS_1 containing H_0 M H^+, (3.000 − H_0) M Na^+ and 3.000 M ClO_4^-, in which $H_0 \approx 1 \times 10^{-3}$ M, was titrated coulometrically, by cathodic reduction of H^+, using the circuit (I), in which

$$\text{Pt} \mid \text{TS} \mid \text{A.E.} \qquad \text{(I)}$$

− constant current source +

A.E. = 3.000 M $NaClO_4$|2.800 M Na^+, 0.100 M Hg_2^{2+}, 3.000 M ClO_4^-|Hg (Pt) is an external auxiliary electrode, connected to TS by means of a salt bridge. TS is the solution resulting from TS_1 by stepwise additions of μ microfaradays through the circuit (I). Here $\mu = n$, where n stands for the micromoles of H^+ consumed by cathodic reduction, eqn. (5) where i is in A and t is in S.

$$\mu = it/0.096487 \qquad (5)$$

After each delivery of current the potential, E_g, of a glass electrode, G.E., is measured by cell (II). In eqn. (6), $h = (n_0 - n)/(1000V_0)$ in which n_0 is the number of micromoles of H^+ in V_0 cm^3 of TS_1. From eqn. (6), transformed into a Gran[10] function, E^0_g is determined. It will be of use in the final stage.

$$\text{G.E.} \mid \text{TS} \mid \text{R.E.} \qquad \text{(II)}$$

$$E_g = E^0_g + 59.16 \log h \qquad (6)$$

Second stage. In the resulting V_0 cm^3 of nearly neutral solution TS_2 of composition 3.000 M $NaClO_4$ the second stage takes place by stepwise additions of V cm^3 of a solution T_2, A_1 M $C_2O_4^{2-}$, (3.000 + 2 A_1) M Na^+, 3.000 M ClO_4^-, at $-7 < \log h < -6$ to avoid the hydrolysis of $C_2O_4^{2-}$. After each addition of T_2 to TS_2 the emf of the cell (III) was measured until it remained constant to within 0.02 mV, during at least 15 minutes. In cell (III) TS is the solution resulting from mixing TS_2 and T_2, while R.E. = 3.000 M $NaClO_4$|0.010 M Ag^+, 2.990 M Na^+, 3.000 M ClO_4^-|AgCl, Ag is an external reference electrode connected to TS by a salt bridge.

$$\text{(Pt,Au)Hg} \mid Hg_2C_2O_4\text{(s)} \mid \text{TS} \mid \text{R.E.} \qquad \text{(III)}$$

The emf, E, of cell (III) may be written as in eqn. (7) in which $a = [C_2O_4^{2-}] = VA_1/(V_0 + V)$. In eqn. (7) we have used concentrations instead of activities for the reasons given earlier. For the same motivation the liquid junction potential has been neglected. Eqn. (7) may be rearranged in the form of Gran[10] diagrams through which E^0 is determined as well as A_0 in TS_3, *i.e.* A_0 M $C_2O_4^{2-}$, (3.000 + 2 A_0) M Na^+, 3.000 M ClO_4^-, which is the solution resulting from the second stage.

$$E = E^0 - 29.58 \log a \qquad (7)$$

Final stage. This consists of the acidification of solution TS_3. We have performed it using an advantageous titration technique illustrated elsewhere,[11] to obtain the data plotted in Figs. 1 and 2. This graphical representation, consisting of multiple curves having different shapes and spacings from one another, in our opinion is better suited than a single curve describing the formation function Z (log a). It demonstrates convincingly the agreement between the data from the glass and the oxalate electrodes. Furthermore it proves that the latter performs properly even in acidic regions, where $h \approx H$ so that the former becomes of little use. The solution TS_3 was acidified to a predetermined value of the ratio $Q = H/A$, by the addition of a weighed amount of a suitable solution. The titration was carried out by employing a titrant having the same value of Q, but higher values of H and A. After each addition the emfs of cells (II) and (III) were measured. Since E^0_g and E^0 had been determined in the previous stages, it was possible to calculate a and h, from eqns. (6) and (7), obtaining two independent sets of data (available as ESI) from which the experimental functions (8) and (9) were constructed. They are plotted (symbols) in Figs. 1 and 2 respectively. If the normalised variables $u = K_1a$ and $v = K_1h$ are introduced into eqns. (8) and (9), as well as in the expression of Q, we obtain eqn. (10) and the normalised forms of the functions (8) and (9), *i.e.* (11) and (12). The theoretical curves (11) have been superposed on the experimental data represented by function (8) in Fig. 1, whereas the model curves (12) have been superposed on the experimental

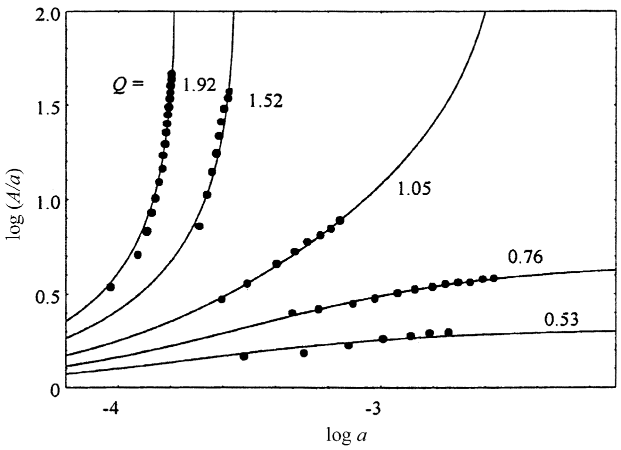

Fig. 1 The experimental data (symbols) log $(A/a)_Q$ *vs.* log a (eqn. (8)) at constant values of $Q = H/A$ (see ESI). The full curves represent the normalised function log (1 + v) *vs.* log u (eqn. (11)). For the best fit log K_1 = 3.83 ± 0.01 is obtained.

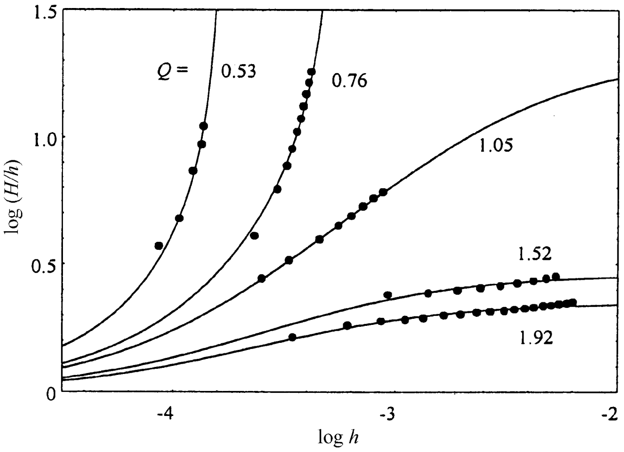

Fig. 2 The experimental data (symbols) log $(H/h)_Q$ *vs.* log h (eqn. (9)) at constant values of $Q = H/A$ (see ESI). The full curves represent the normalised function log (1 + u) *vs.* log v (eqn. (12)). For the best fit log K_1 = 3.83 ± 0.01 is obtained.

$$\log (A/a)_Q \ vs.\ \log a \qquad (8)$$

$$\log (H/h)_Q \ vs.\ \log h \qquad (9)$$

$$Q = H/A = [h(1 + K_1a)]/[a(1 + K_1h)] = v(1 + u)/[u(1 + v)] \qquad (10)$$

$$\log (1 + v) \ vs.\ \log u \qquad (11)$$

$$\log (1 + u) \ vs.\ \log v \qquad (12)$$

Table 1 Survey of the oxalic acid formation constants obtained in 3 and 2 M $NaClO_4$ (this work) and in 1 M $NaClO_4$ (reference 1). The results are also given in molal (m) units. In the last row the extrapolated values are reported

$[NaClO_4]$/M	$\log K_1$	$\log K_2$	$[NaClO_4]/m$	$\log {}^mK_1$	$\log {}^mK_2$
1.000	3.57 ± 0.02	1.00 ± 0.03	1.050	3.55 ± 0.02	0.98 ± 0.03
2.000	3.57 ± 0.02	1.14 ± 0.03	2.207	3.49 ± 0.02	1.07 ± 0.03
3.000	3.81 ± 0.02	1.14 ± 0.02	3.496	3.73 ± 0.02	1.07 ± 0.02

Extrapolated values: $\log {}^0K_1 = 4.22 \pm 0.05$; $\log {}^0K_2 = 1.3_5 \pm 0.1$.

map (9) in Fig. 2. The fit is excellent for the two sets of data which are consistent with the value $\log K_1 = 3.83 \pm 0.01$, determined in a previous study.[1]

Determination of the second protonation constant, K_2, of $C_2O_4^{2-}$

The measurements which follow are even more relevant to the scope of this work aimed at elucidating the complex formation between UO_2^{2+} and $C_2O_4^{2-}$. The equilibrium constant, K_2, of reaction (3) is not easily determined because of its low value, which makes oxalic acid one of the strongest, within the partially dissociated acids. At $\log h > -1$, $H_2C_2O_4$ is the predominant form of oxalate, thus its formation constant must be accurately known if measurements are performed in that acidity range. This demand cannot adequately be answered by increasing the precision of the measurements of h, because, at high acidity, $H \approx h$. Thus the concentration of bound ligand, $H - h$, cannot be evaluated with due precision. Conversely the free oxalate may be determined with great accuracy in acidic solution.

In this section the measurements with the glass and oxalate electrodes, in solutions of acidity in the interval $10^{-6} < h < 3$ M, are treated. The experiments were carried out in three stages. The first two were identical to those described in the previous section and produced values of E^0_g and E^0. The third stage was carried out in a solution TS_4 of composition H M H^+, A M OX, $(3.000 + 2A - H)$ M Na^+, 3.000 M ClO_4^-, in which OX indicates oxalate in all its forms. In order to favour the formation of oxalic acid and also to test the oxalate electrode under extreme conditions of acidity, in TS_4 H was varied between 0 and 3 M. This implies a change of the ionic medium from 3 M $NaClO_4$ to 3 M $HClO_4$, *i.e.* the replacement of Na^+ by H^+, with obvious consequences on the activity coefficients. The measurements were carried out by means of the junctionless cell (IV) whose

$$(Pt,Au)Hg/Hg_2C_2O_4(s) \mid TS_4 \mid G.E. \qquad (IV)$$

emf may be written as in eqn. (13) where the last two terms in

$$*E = E_g - E = E^0_g - E^0 + 29.58 \log(h^2a) + 29.58(2\Delta \log f_+ + \Delta \log f_{2-}) \qquad (13)$$

parentheses account for the variation of the activity coefficients of H^+ and of $C_2O_4^{2-}$, respectively, on passing from 3 M Na^+ to 3 M H^+, in TS_4. By combining eqns. (2), (3), (13) with the mass balance for oxalate, eqn. (14) is obtained. In eqn. (14)

$$Y = *E - *E^0 - 29.58 \log A = -29.58 \log(K_1K_2) - 29.58 \log[1 + K_2h^{-1} + (K_1K_2)^{-1} + (K_1K_2)^{-1}h^{-2}] + 29.58(2\Delta \log f_+ + \Delta \log f_{2-}) \qquad (14)$$

$*E^0 = E^0_g - E^0$ is determined in the course of the first two stages of the titration. Using the Specific Interaction Theory,[5] the relation (15) may be derived where $\Delta\varepsilon$ indicates the difference of the interaction coefficients, eqn. (16). Introducing eqn. (15) into eqn. (14) we finally obtain eqn. (17).

$$29.58(2\Delta\log f_+ + \Delta\log f_{2-}) = 29.58\ \Delta\varepsilon h \qquad (15)$$

$$\Delta\varepsilon = \varepsilon(C_2O_4^{2-}, H^+) - \varepsilon(C_2O_4^{2-}, Na^+) \qquad (16)$$

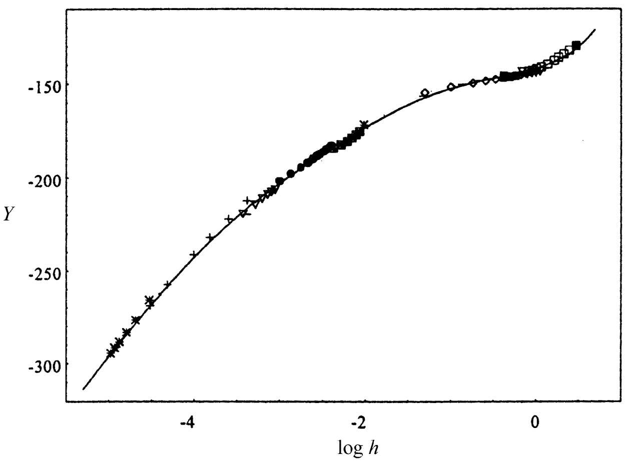

Fig. 3 Representation of the function (17), $-Y(-\log h)$. The symbols refer to the experimental data $Y = E^* - E^0 - 29.58 \log A$ *vs.* $\log h$ (series I of Table 3 (ESI) in 3 M $NaClO_4$). The full curve has been calculated by assuming the following values: $\log K_1 = 3.81$; $\log K_2 = 1.14$ and $\Delta\varepsilon = 0.17\ M^{-1}$.

$$Y = *E - *E^0 - 29.58 \log A = -29.58 \log(K_1K_2) - 29.58 \log[1 + K_2h^{-1} + (K_1K_2)^{-1} + (K_1K_2)^{-1}h^{-2}] + 29.58\ \Delta\varepsilon h \qquad (17)$$

The experimental data Y ($\log h$) (see ESI) are plotted in Fig. 3. The first member of eqn. (17), consisting of known quantities, is plotted (symbols) *vs.* $\log h$, which at $h > 0.1$ M has been calculated as $\log(H - 2A)$, since the liquid junction potential becomes too large to accurately be accounted for by means of eqn. (18), given in the next section. The full curve fitting of the data has been calculated by introducing in the second member the following values, listed in Table 1, in molar and molal units, in three ionic media, and at $I = 0$ M: $\log K_1 = 3.81 \pm 0.02$, $\log K_2 = 1.14 \pm 0.02$ and $\Delta\varepsilon = 0.17 \pm 0.02\ M^{-1}$. Unfortunately it was not possible to refine the results by the least squares program LETAGROP,[12] as we did in the following section. In fact this program, developed for interpreting measurements in the presence of an ionic medium, is not predisposed to consider data obtained in mixtures of electrolytes, which demand simultaneous evaluation of the equilibrium constants and of the activity factor changes.

On the complex formation equilibria between UO_2^{2+} and $C_2O_4^{2-}$ at $\log h \geq 2$

The study on the complex formation between UO_2^{2+} and $C_2O_4^{2-}$ is potentially complicated by the formation of ternary species, in the acidity range in which hydrolysis takes place, as seems probable on the basis of exploratory experiments. Thus we have chosen to divide it into two parts: first we have investigated the range $\log h \geq -2$, in order to hinder hydrolysis of the uranyl oxalate complexes and to favour the formation of binary species. This study has been carried out potentiometrically in 2 and 3 M $NaClO_4$, in an air thermostat at 25.00 ± 0.02 °C. The acidity has gradually been decreased to a level of $\log h \leq -7$. We have thus obtained definite evidence of the formation of ternary, polynuclear complexes, bearing UO_2^{2+}, $C_2O_4^{2-}$ and OH^- ions. A report on this further investigation will follow

Table 2 Survey of the formation constants of the mononuclear $UO_2(C_2O_4)_p^{(2-2p)+}$, $p = 1$, 2 or 3. The results of the present work, in 3 and 2 M $NaClO_4$, have been combined with those of refs. 7 and 14, in 1 M $NaClO_4$, to extrapolate β_n to zero ionic strength

$[NaClO_4]$/M	log β_1	log β_2	log β_3	$[NaClO_4]$/m	log $^m\beta_1$	log $^m\beta_2$	log $^m\beta_3$	Ref.
1.000	6.02 ± 0.03	10.55 ± 0.06	14.0 ± 0.03	1.050	6.00 ± 0.03	10.52 ± 0.06	13.9 ± 0.3	1
1.000	5.99 ± 0.03	10.64 ± 0.06	11.0 ± 0.02	1.050				14
2.000	6.20 ± 0.02	11.21 ± 0.02	14.9 ± 0.01	2.207	6.16 ± 0.02	11.12 ± 0.04	14.8 ± 0.01	p.w.
3.000	6.39 ± 0.01	11.52 ± 0.02	15.2 ± 0.01	3.496	6.33 ± 0.01	11.39 ± 0.02	15.0 ± 0.01	p.w.

Values extrapolated to zero ionic strength by means of the Specific Interaction Theory: log $^0\beta_1 = 7.38 \pm 0.07$, log $^0\beta_2 = 11.7_2 \pm 0.1$, log $^0\beta_3 = 13.6 \pm 0.2$. p.w. = Present work.

shortly. However in the present study the experimental conditions have been varied within the following intervals: $-2.3 < \log B < -1.5$; $-2 < \log h < -1$ and $-3.5 < \log A < -1.5$. The limits of the concentrations B and A have been imposed by the low solubility of $Na_2C_2O_4$ in 2 and 3 M $NaClO_4$. The experiments were carried out as titrations, which were divided into three stages. The first and the second stages were as described in the previous sections and were aimed at determining the values of E^0_g and E^0. To the resulting solution TS_4 a weighed amount of a suitable UO_2^{2+} solution was added to attain a predetermined value of B, without varying the 3 M level of $[ClO_4^-]$, obtaining a solution of composition TS_5, *i.e.* B M UO_2^{2+}, H_0 M H^+, A_0 M OX $(3.000 - 2B - H_0 + 2A_0)$, M Na^+, 3.000 M ClO_4^-. This was titrated by two solutions T_3 and T_4 of compositions A_T M $C_2O_4^{2-}$, $2A_T$ M Na^+ and $2B$ M UO_2^{2+}, H_T M H^+, $(6.000 - 2B - H_T)$, M Na^+, 6.000 M ClO_4^-. The addition of equal volumes of T_3 and T_4 to TS_5 modified A and H, without changing B and $[ClO_4^-]$.

The emfs of cells (II) and (III) are expressed by eqns. (6) and (7), in which however the liquid junction potential, E_j, has to be introduced. It accounts for the differences of composition between the test solution and the ionic medium 3 M $NaClO_4$. It is easily verified that the liquid junction potential due to the replacement of Na^+ by UO_2^{2+}, as well as that originating from the excess of $[Na^+]$ over the 3 M level, are negligible, because of the limited values reached by B and A. Conversely, for the most acidic solutions, the junction potential due to the replacement of Na^+ by H^+ has to be accounted for, according to the simple relationship[13] (18) in which E_j is expressed in mV if h is given in molar units.

$$E_j = -16.8\,h \tag{18}$$

The $E\,(A, H)_B$ and $E_g\,(A, H)_B$ data have accordingly been corrected for E_j before recalculating them in the form of the function Z (log h), given by eqn. (19) where Z is the average

$$Z = (A - \alpha a)/B \tag{19}$$

number of oxalate ions per uranium atom and $\alpha = (1 + K_1h + K_1K_2h^2)$ is a quantity proportional to the oxalate bound to H^+ and not bound to UO_2^{2+}. The Z (log a) data (see ESI) plotted in Fig. 4 suggest the formation of mononuclear binary species, only bearing uranium and oxalate. In fact measurements obtained at different B and H fall on the same line. Furthermore data at varying B, obtained from titrations in which we aimed at maximising the ratio A/B, by varying B between 0 and 0.03 M (since A could not be increased above 0.01 M for solubility reasons) fall, over the same curve, equally well. Thus the equilibria between UO_2^{2+} and $C_2O_4^{2-}$ at $\log h \geq -2$ may be described by reaction (1). Z may then be written as in eqn. (20).

$$Z = (A - \alpha a)/B = \Sigma p\beta_p a^p / \Sigma\beta_p a^p \tag{20}$$

The values of p and of the formation constants β_p in eqn. (20) have been determined by simple graphical methods and refined by the least squares program LETAGROP, version Etitr,[12] obtaining substantially the same results.

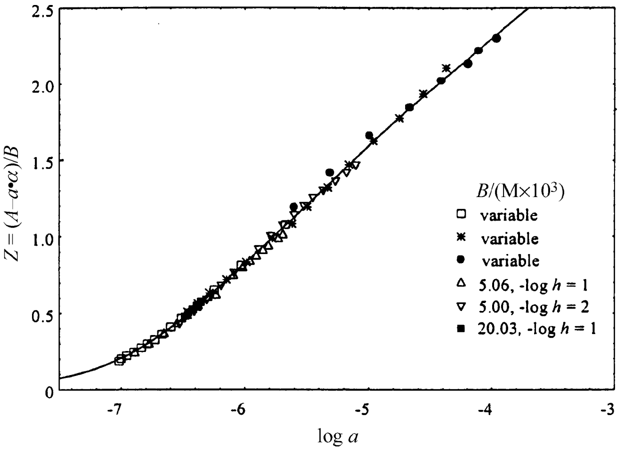

Fig. 4 Representation of the function (20): Z (log a). The symbols indicate the experimental data collected at various B, H and A, in 3 M $NaClO_4$ (series I of Table 4 (ESI)). The full curve has been calculated with the following values of the equilibrium constants: log $K_1 = 3.82$, log $K_2 = 1.14$, log $\beta_1 = 6.39$, log $\beta_2 = 11.52$ and log $\beta_3 = 15.21$.

The full curve in Fig. 4 has been calculated by assuming the values of the equilibrium constants given in the fourth row of Table 2, where the results of the present study, in 2 and 3 M $NaClO_4$ are summarised, together with those obtained by Vasca *et al.*[1] and by Havel,[14] in 1 M $NaClO_4$, for the sake of comparison.

Extrapolation of the result to zero ionic strength

Method I. In the following calculation the data in 1 M $NaClO_4$ obtained by Vasca *et al.*[1] have also been taken into consideration. By applying the SIT to the formation constants $^mK_1$ and $^mK_2$, expressed in molal units, eqns. (21) and (22) are

$$\chi_1 = \log {}^mK_1 + 4D - \varepsilon(H^+, ClO_4^-)\,m = \log {}^0K_1 + [\varepsilon(Na^+, HC_2O_4^-) - \varepsilon(Na^+, C_2O_4^{2-})]m \tag{21}$$

$$\chi_2 = \log {}^mK_2 + 2D + \varepsilon(H^+, ClO_4^-)\,m = \log {}^0K_2 + [\varepsilon(NaClO_4, H_2C_2O_4) - \varepsilon(Na^+, HC_2O_4^-)]m \tag{22}$$

obtained. If we plot the first members of eqns. (21) and (22) *vs.* m, the molal concentration of ClO_4^-, we obtain the values of log $^0K_1$ and log $^0K_2$ extrapolated at zero ionic strength, given in Table 1.

Method II. A similar treatment can be made of the formation constants of the uranyl oxalate complexes. Eqn. (23) relates the

$$^0\beta_p = {}^m\beta_p\delta^{-p}\,(\gamma_p\gamma_b^{-1}\gamma_a^{-p}) \tag{23}$$

constants valid at zero ionic strength, $^0\beta_p$, to the ones valid in the ionic media, $^m\beta_p$. In eqn. (23) δ = molality/molarity, γ_p is the activity coefficient of the species $UO_2(C_2O_4)_p^{(2-2p)+}$ in molal units, γ_b the activity coefficient of UO_2^{2+} and γ_a that of $C_2O_4^{2-}$.

Table 3 Interaction coefficients, in kg mol^{-1}, obtained by measurements in three ionic media

ε(Na$^+$, $C_2O_4^{2-}$) = 0.05, ε(H$^+$, $C_2O_4^{2-}$) = 0.15, ε(Na$^+$, $HC_2O_4^-$) = 0.12, ε(Na$^+$, $UO_2(C_2O_4)^0$) = 0.23, ε(Na$^+$, $UO_2(C_2O_4)_2^{2-}$) = 0.56, ε(Na$^+$, $UO_2(C_2O_4)_3^{4-}$) = 0.17

If we substitute, in eqn. (23), the expression for γ suggested by the SIT, we obtain eqn. (24) in which $\varepsilon_b = \varepsilon(UO_2^{2+}, ClO_4^-)$,

$$\log {}^0\beta_p = \log {}^m\beta_p + 4p(3-p)D - (\varepsilon_b + p\varepsilon_a - \varepsilon_p)m \quad (24)$$

$\varepsilon_a = \varepsilon(Na^+, C_2O_4^{2-})$ and $\varepsilon_p = \varepsilon(UO_2(C_2O_4)_p^{(2-2p)+}, Na^+)$. Eqn. (24) shows that plots of $\log {}^m\beta_p + 4p(3-p)D$ *vs.* m, should appear as straight lines giving values of $\log {}^0\beta_p$ as intercepts on the ordinate and $(\varepsilon_b + p\varepsilon_a - \varepsilon_p)$ as the slopes. The results of the extrapolation are given in Table 2. In Table 3 a list of useful ε values determined in this work is also given.

Discussion

The measurements summarised graphically in Figs. 2 and 3 evidence that the (Pt,Au)Hg–$Hg_2C_2O_4$ electrode exhibits Nernstian behaviour. The reaction (4) has proved to be rapid and reversible, adequate for equilibrium studies and for direct analysis. The stability of $Hg_2C_2O_4$ seems satisfactory and the oxidation of $C_2O_4^{2-}$ by Hg_2^{2+} does not take place significantly if the electrode is protected from direct daylight. Its lifetime is limited to about 5 weeks, but this does not constitute a serious problem for applications of the type shown in this work, which usually last for a shorter time. On the other hand its preparation is simple and scarcely time consuming. The advantages afforded are evident if we examine for example the extreme conditions of acidity, up to 3 M $HClO_4$, under which we have tested the electrode. Under similar conditions, measurements of h are not significant since H and h practically coincide.

We also point out the reliability of the SIT in evaluating the change in activity factors. A striking example is represented by the adequacy of eqn. (17) to explain the measurements of the glass and oxalate electrodes in terms of K_1, K_2 and $\Delta\varepsilon$. It is worth noticing that the magnitude of the last term in eqn. (17) attains a value larger than 20 mV, in 3 M $NaClO_4$, and could simulate the formation of a species with 3 protons, $H_3C_2O_4^+$, if the SIT did not allow us to separate the effect (on the potential of the electrodes) due to complex formation from that due to the change in activity factors. This procedure is inevitable when passing from a constant ionic medium to a mixture of electrolytes, *i.e.* as for instance in the case of weak complexes in which the formation of the limiting species requires a large value of the concentration ratio ligand/central ion, and thus a substantial replacement of the medium ions. The reliability of the evaluation of the activity coefficient changes is corroborated by the consistency of $\delta\varepsilon$ in the two ionic media studied. Ultimately, as a by-product of the results pursued, we have also determined a number of interaction coefficients which will be useful in the continuation of this work.

Uranium is a strategic element. Thus the physico-chemical properties of its solutions have been the object of extensive studies. The equilibria between uranium(VI) and the hydroxyl ion have been studied by several authors and are fairly well known.[15] Less known is the hydrolysis of U^{IV}.[15] Complex formation with carbonates of $U^{VI,V,IV}$ has also been systematically investigated, particularly in the course of the last twenty years.[9] On the contrary, little attention has been devoted to the oxalate complexes. The study which has been credited as the most reliable was published thirty years ago, by Havel.[14] He interpreted his accurate spectrophotometric data, in 1 M $NaClO_4$, in terms of the formation of three mononuclear species having $\log \beta_1 = 5.99 \pm 0.03$, $\log \beta_2 = 10.64 \pm 0.06$ and $\log \beta_3 = 11.0 \pm 0.2$. It is immediately evident that the third complex has a formation constant about 2–3 logarithmic units smaller than expected. This finding has recently been used[9] to hypothesise that the third oxalate ion does not find sufficient room in the equatorial plane of the uranyl ion, thus it co-ordinates "head on", *i.e.* through two oxygen atoms bound to the same carbon atom, forming a four membered ring, as it has been found in some solid compounds[9] containing oxalate and uranyl. Conversely the present results corroborate the assumption of three identically co-ordinated oxalate ions.

Table 4 Evaluation of $\log \beta_n$ values by correlation between $\log \beta_n$ and $\Delta\nu_1$ (cm^{-1}) determined in ref. 16. $\Delta\nu_1$ is the shift of the frequency of the symmetrical stretching vibration corresponding to O=U=O, due to co-ordination of $C_2O_4^{2-}$ in the equatorial plane of UO_2^{2+}

n	$\log \beta_n$	$\Delta\nu_1$/cm^{-1}	Value of $\log \beta_n$
1	$-0.52(\Delta\nu_1) - 1.61$	−15	6.2
2	$-0.50(\Delta\nu_1) - 4.10$	−30	10.9
3	$-0.46(\Delta\nu_1) - 5.86$	−45	14.8

In 1992 Nguyen-Trung *et al.*[16] reported an extremely interesting study on the Raman spectra of the dioxouranium(VI) ion. The wavenumber of the symmetrical stretching vibration ν_1 corresponding to O=U=O is shifted for each ligand co-ordinated in the equatorial plane of uranium. The shift when passing from UO_2^{2+} to the complex species $UO_2(C_2O_4)_n$ (n = 1–3) was used to estimate the formation constants of the complexes (Table 4). Examining Table 4, we can observe a substantial correspondence between the experimental results obtained in the present work and the values calculated (valid in varying ionic strength) according to ref. 16.

For the sake of comparison the formation constants of the uranyl complexes with oxalate are given in Table 2. An intriguing question is whether polynuclear and ternary species are formed in the dioxouranium(VI)-oxalate system. Polynuclear complexes are not reported in the literature. However, we have evidence of the formation of mixed polynuclear species in which two uranyl ions, bearing oxalate, are bridged through hydroxide. It is our intention to investigate complex formation between the oxalate ion and uranium in its various oxidation states systematically, varying as much as possible the experimental conditions. Our ultimate goal, in addition to the applied aspects, is to contribute relevant information to compare and possibly correlate the mechanisms of complex formation of oxygen-containing ligands such as OH^-, CO_3^{2-} and $C_2O_4^{2-}$.

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