The Hydrolysis of Metal Ions. Part 2.[1] Dioxouranium(VI)

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The hydrolysis of dioxouranium(VI) has been investigated by potentiometric titration at 25 °C in 0.10 mol dm^{-3} K[NO$_3$]. Data treatment by advanced computer techniques indicates the presence of the species $[UO_2(OH)]^+$, $[(UO_2)_2(OH)_2]^{2+}$, $[(UO_2)_3(OH)_4]^{2+}$, $[(UO_2)_3(OH)_5]^+$, and $[(UO_2)_4(OH)_7]^+$ under the experimental conditions used; the $-\log \beta_{pq}$ values of these species have been determined to be 5.50 (0.03), 5.89 (0.004), 12.31 (0.03), 16.46 (0.01), and 22.76 (0.02), respectively, the estimated standard deviations being given in parentheses. These results have been obtained for the narrow range of total initial uranium concentration of 0.185×10^{-3}—1.853×10^{-3} mol dm^{-3}, as required by the low value of the ionic strength used. The significance of this restricted range is discussed.

THE hydrolysis of the dioxouranium(VI) ion [henceforth referred to as the uranium(VI) ion] has been the subject of investigations for nearly 30 years.[2-16] An examination of the various results reveals that this system is extremely complex because of the large extent of hydrolysis which occurs before precipitation and several polymeric species are apparently produced simultaneously. Although the species $[(UO_2)_2(OH)_2]^{2+}$ and $[(UO_2)_3(OH)_5]^+$ appear to be well documented as major ones,[17] it appears unlikely that these species alone can account for the complex hydrolytic behaviour.

In keeping with the aims of this series,[1] we have re-investigated this system. In this instance, measurements have been limited to the ionic medium 0.10 mol dm^{-3} potassium nitrate.

EXPERIMENTAL

Reagents.—Unless otherwise stated, all the reagents were Merck G.R. quality and were used without further purification. The source of uranium was undepleted Nuclear Grade uranium(VI) nitrate 6-hydrate. Uranium was determined spectrophotometrically using 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol.[18]

pH *Interpretation.*—The pH measurements were carried out using the previously described equipment.[1] In Part 1 [1] the pH meter was calibrated using a method essentially the same as that of McBryde [19] which assumes that the hydrogen-ion concentration, $[H^+]$, equals $10^{-pH}/\lambda$, where λ is determined by potentiometric titration of a standardised nitric acid solution (in 0.10 mol dm^{-3} K[NO$_3$]). In the case of Cu^{II} this method was satisfactory but somewhat unnecessary because the hydrogen-ion concentrations were generally about two orders of magnitude less than that of the metal ion, which made the numerical results insensitive to the value of λ. Thus in this case the error-square sum was very nearly independent of λ.

However, in the case of the uranium(VI) hydrolysis data the proton and metal concentrations are of comparable magnitude and, for a given speciation scheme, the minimum error-square sum is very dependent on the value of λ chosen (see Discussion section). It was therefore concluded that there was sufficient information to enable the value of λ to be refined together with the other parameters. Accordingly, the necessary changes were made to our version [1] of the computer program [20,21] MINIQUAD 75 to achieve this (see Appendix).

The refined values of λ varied very little for the various models tested if the models agreed reasonably well with the experimental data. For the model finally chosen the value of λ was 0.850. Use of this value assumes that, for all the titrations, compositional changes have a negligible effect on λ. This is only an approximation and the refinement of λ spreads the effects of this approximation over all the titration points. The difference between the present value of 0.850 and the value experimentally determined in the absence of a hydrolysing metal ion (as in the case of Cu^{II}), namely 0.914, is doubtless the result of this approximation. Fortunately, the numerical analysis of the copper(II) data did not require a precise value of λ.

We believe that this method of converting pH values into hydrogen-ion concentrations, which is based directly on the experimental data, is superior to methods which involve assumptions about activity factors and liquid-junction potentials. Although arrived at independently, this approach has been mentioned by Hietanen *et al.*[11] and used by Childs and Perrin.[22]

Base Addition and Titration Procedure.—The procedure previously used [1] was followed. All the titrations were carried out at 25.0 ± 0.1 °C in 0.10 mol dm^{-3} K[NO$_3$]. Since the base solution was also 0.10 mol dm^{-3} in K[NO$_3$] the concentration of the ionic medium remained constant throughout the titrations. This low value of the ionic strength allowed examination of only a very narrow range of total uranium(VI) concentrations. The significance of this is discussed below. The contribution of the ionisation of water to the proton mass balance was ignored since it is negligible in the pH range examined. Some details of the titrations are given in Table 1; full details are available on request.

TABLE 1

Summary of titrations of uranium(VI) at 25.0 °C in 0.10 mol dm^{-3} potassium nitrate

Total (initial) uranium concentration (10^{-3} mol dm^{-3})	pH Range	Number of points
1.853	3.208—5.293	65
0.926	3.503—5.496	48
0.463	3.794—5.040	44
0.185	4.184—5.911	42

RESULTS

The convention previously adopted [1] for the reactions (1) defines the stoicheiometric equilibrium constants as (2).

$$p[UO_2]^{2+} + qH_2O \rightleftharpoons [(UO_2)_p(OH)_q]^{(2p-q)+} + qH^+ \qquad (1)$$

$$\beta_{pq} = [(UO_2)_p(OH)_q{}^{(2p-q)+}][H^+]^q/[UO_2{}^{2+}]^p \qquad (2)$$

The various species are referred to by their formulae or by (p,q) pairs.

Initially, the systematic approach previously used for copper(II) [1] was attempted using as the base model the two species (2,2) and (3,5). This approach was unsuccessful presumably because the complexity of the system allowed the existence of many local minima in the error-square sum. In these instances, excellent fits to the data could be obtained but the imprecision in the $-\log \beta_{pq}$ values, as indicated by the estimated standard deviations which were often grossly in excess of 10%, was too great to be acceptable. A trial-and-error approach was then adopted, and ultimately a number of models was refined consisting of various combinations of the species (1,1), (2,2), (3,4), (3,5), (4,6), and (4,7), together with previously published models. These models (Table 2) mainly consist of various groups of the core-plus-link species $[(UO_2)_n(OH)_{2n-2}]^{2+}$, and the two further deprotonated species $[(UO_2)_3(OH)_5]^+$ and $[(UO_2)_4(OH)_7]^+$, in the presence and absence of the (1,1) monomer, $[UO_2(OH)]^+$. Note that the number of species in the species ' list ' must be kept as low as possible or the numerical analysis becomes unmanageable; thus for N species the total number of model combinations is $2^N - 1$.

TABLE 2

Comparison of models of uranium(VI) hydrolysis *

Model number	Model	$-\log \beta_{pq}$	Estimated standard deviation of $-\log \beta_{pq}$	Estimated relative standard deviation of β_{pq} (%)	10^{10}-Error-square sum	R
1	(2,2)	5.83	0.003	0.6	25.2	0.0025
	(3,5)	16.28	0.006	1.4		
2	(1,1)	5.78	0.10	23.2	22.9	0.0024
	(2,2)	5.84	0.005	1.1		
	(3,5)	16.26	0.007	1.6		
3	(2,2)	7.02	0.27	62.7	1 063.2	0.0198
	(3,4)	11.21	0.02	5.0		
4	(1,1)	model fails: (1,1) and (2,2) rejected				
	(2,2)					
	(3,4)					
5	(2,2)	model fails: (3,4) rejected				
	(3,4)					
	(3,5)					
6	(2,2)	5.84	0.006	1.4	23.8	0.0024
	(3,4)	12.84	0.21	47.4		
	(3,5)	16.28	0.007	1.5		
	(4,6)	19.31	1.22	281.7		
7	(1,1)	model fails: (4,6) rejected				
	(2,2)					
	(3,4)					
	(3,5)					
	(4,6)					
8	(2,2)	5.83	0.003	0.8	8.3	0.0014
	(3,4)	12.72	0.09	21.5		
	(3,5)	16.59	0.02	5.8		
	(4,6)	18.05	0.04	9.4		
	(4,7)	22.72	0.02	5.8		
9	(1,1)	5.63	0.06	13.8	6.4	0.0013
	(2,2)	5.87	0.006	1.5		
	(3,4)	12.41	0.05	11.8		
	(3,5)	16.51	0.02	5.0		
	(4,6)	18.47	0.14	31.6		
	(4,7)	22.73	0.02	5.4		
10	(2,2)	model fails: (3,4) rejected				
	(3,4)					
	(4,6)					
11	(1,1)	model fails: (1,1) and (3,4) rejected				
	(2,2)					
	(3,4)					
	(4,6)					
12	(1,1)	5.50	0.03	7.2	6.7	0.0013
	(2,2)	5.89	0.004	0.9		
	(3,4)	12.31	0.03	6.6		
	(3,5)	16.46	0.01	3.0		
	(4,7)	22.76	0.02	5.4		
13	(2,2)	5.85	0.004	0.9	13.8	0.0018
	(3,4)	12.34	0.04	10.4		
	(3,5)	16.43	0.02	3.7		
	(4,7)	22.92	0.004	8.8		
14	(1,1)	5.60	0.06	13.0	15.8	0.0020
	(2,2)	5.84	0.004	0.9		
	(3,5)	16.35	0.01	3.1		
	(4,7)	23.04	0.05	11.9		
15	(1,1)	5.80	0.10	24.1	21.8	0.0023
	(2,2)	5.86	0.006	1.4		
	(3,4)	12.84	0.15	35.0		
	(3,5)	16.27	0.006	1.5		
16	(2,2)	model fails: (3,4) and (4,6) rejected				
	(3,4)					
	(3,5)					
	(4,6)					
	(5,8)					
17	(2,1)	model fails: (2,1), (3,4) and (4,6) rejected				
	(2,2)					
	(3,4)					
	(3,5)					
	(4,6)					
18	(2,1)	model fails: (2,1) and (3,4) rejected				
	(2,2)					
	(3,4)					
	(3,5)					

* A species is rejected when the value of β_{pq} becomes negative.

The criteria for the acceptability of any given model must ultimately be subjective.[1] The previous criteria used for the selection of the ' best ' model (Part 1) are the *simultaneous* existence of: (*a*) standard deviations (relative percentage) of all the constants of *ca.* $< 10\%$; (*b*) a value of the goodness of fit parameter, the R factor, of *ca.* 0.001 (for 150—200 data points). These were applied again here and an examination of Table 2 clearly indicates that model 12, consisting of the five species (1,1), (2,2), (3,4), (3,5), and (4,7), is the ' best ' model; that is, it is the only one which meets these criteria. The only comparable model is 9 which additionally contains the (4,6) species. However, although its presence slightly improves the goodness of fit, uncertainties are introduced into the values of all the constants, as indicated by the increased estimated standard deviations. It must be concluded that the present data do not provide sufficient evidence for the existence of the (4,6) species. The other models tested are also included in Table 2 to enable further comparison.

Models 13—15 were calculated in an attempt to reduce the number of species in the ' best ' model to four. Thus, the three least certain species, that is (1,1), (3,4), and (4,7), were removed from model 12 one at a time. Clearly, such alterations in the models have a deleterious effect on both the estimated standard deviations and the goodness of fit. It is thus difficult to avoid the conclusion that all five species need to be included in the ' best ' model.

One important aspect of the numerical analysis required for the present kind of data treatment is the problem of just how close the initial estimates of the β_{pq} values need to be to the ' true ' values. One of the features of MINIQUAD 75 is that initial guesses need only be very approximate, but we have found that this applies only in relatively simple systems. For the uranium(VI) system the value of the initial guesses needed to be quite close to the ' true ' values to avoid unsatisfactory results. This is not seen to be a limitation of MINIQUAD 75 but a problem inherent in the numerical analysis of complex systems.

TABLE 3

Experimentally determined and empirical estimated values of some hydrolysis constants

Species	$-\log \beta_{pq}$ Experimental	$-\log \beta_{pq}$ Estimated
$[Cu_3(OH)_4]^{2+}$	21.62	21.98
$[(UO_2)_3(OH)_4]^{2+}$	12.31	11.78
$[(UO_2)_3(OH)_5]^{+}$	16.46	17.28
$[(UO_2)_4(OH)_7]^{+}$	22.76	23.17

The success of the approximation method previously used[1] [equation (3)] can be judged from Table 3, where

$$\log \beta_{pq} \sim q \log \beta_{11} - (p - 1)(2 \log \beta_{11} - \log \beta_{22}) \qquad (3)$$

estimated and refined values of $-\log \beta_{pq}$ for $[Cu_3(OH)_4]^{2+}$, $[(UO_2)_3(OH)_4]^{2+}$, $[(UO_2)_3(OH)_5]^{+}$, and $[(UO_2)_4(OH)_7]^{+}$ are given, based on the finally adopted values of $-\log \beta_{11}$ and $-\log \beta_{22}$ (Part 1[1] and present work). The difference in values is always less than an order of magnitude which provides some evidence that the physical basis of this empirical relation (Part 1) is valid.

The variation of $-\log \beta_{pq}$ in model 12 was examined over a wide range of λ. For $0.75 \leqslant \lambda \leqslant 0.95$ there is very little variation (between 0.06 and 0.78 log units at most, depending on the species) but the estimated standard deviations and the error-square sums become unsatisfactory. Only when $\lambda \geqslant 1.1$ or $\leqslant 0.67$ was model 12 rejected (a β_{pq} became negative). Such model stability is possibly useful as a further criterion for model acceptance, since, in some other models, rejection occurred over a much narrower range of λ. This matter will be further investigated.

DISCUSSION

A comparison of the present results with some previous results is given in Table 4 where the model numbers refer to the schemes listed in Table 2. The most important difference between the investigations is that the present one uses low values of the total uranium(VI) concentrations.

If the error-square sums for models 1 and 12—15 (Table 2) are compared the five species can be ranked in importance as (2,2) ~ (3,5), (4,7), (3,4), and (1,1) in order of decreasing contribution to the present experimental data. The importance of the various species as a function of pH can be gauged from Figure 1 which refers to a total uranium(VI) concentration of 10^{-3} mol dm^{-3}. In these calculations, true equilibrium is assumed to be present; this will not be true at the higher pH values when some supersaturation or precipitation will be present.

From Figure 1 it can be seen that the (1,1) species is always only a minor one. Although the present data require its inclusion, earlier investigations rely on data largely relating to very much higher total uranium concentrations. Under these circumstances the relative contribution of this species to such data is negligible and its frequent omission is understandable.

The (2,1) species has only been detected in that

TABLE 4

Survey of some results of investigations of the hydrolysis reactions of uranium(VI) at 25 °C

Medium[a]	Total uranium concentration range (10^{-3} mol dm^{-3})	$-\log \beta_{pq}$[b]								Model number	Ref.
		(1,1)	(2,1)	(2,2)	(3,4)	(3,5)	(4,6)	(4,7)	(5,8)		
1.5 mol dm^{-3} (Na)SO_4	0.3—40.0			8.20	16.21	22.13	24.56		32.30	16	5,10
3.0 mol dm^{-3} (Na)Cl	0.625—80.0			6.64	12.54	18.07	19.96	24.91		8	9
3.0 mol dm^{-3} (Mg)ClO_4	2.0—1 200		3.81	6.25	*ca.* 13.33	17.18	*ca.* 20.18			17	11
3.0 mol dm^{-3} (Ca)ClO_4	1.0—1 200		3.96	6.20	*ca.* 13.44	16.91				18	11
3.0 mol dm^{-3} (Na)ClO_4	2.0—1 200		3.7	6.02	*ca.* 13.83	16.54	*ca.* 19.21			17	11
3.0 mol dm^{-3} (Na)ClO_4	0.25—100	*ca.* 6.10		6.04	*ca.* 13.21	16.53				15	11
1.0 mol dm^{-3} (K)NO_3	not available		*ca.* 4.16	5.96	*ca.* 12.79	16.21				18	10
3.0 mol dm^{-3} (Mg)NO_3	2.0—100	*ca.* 5.38		6.34		17.37				2	12
5.0 mol dm^{-3} (Mg)NO_3	2.0—100	5.53		6.52		17.76				2	12
1.0 mol dm^{-3} (Na)Cl	1.0—100			6.17	12.33	17.00				5	6
0.5 mol dm^{-3} (K)NO_3	0.8—9.9	5.7		5.92		16.22				2	8
1.0 mol dm^{-3} (Na)ClO_4	1.0—100			5.91		16.43				1	7
0.10 mol dm^{-3} (K)NO_3	0.185—1.853	5.50		5.89	12.31	16.46		22.76		12	This work

[a] The molarity of the medium refers to the anion. [b] The approximations were reported as such, and indicate estimated standard deviations in excess of 20%.[10]

work[10,11] relating to the very highest uranium(VI) concentrations. Attempts at incorporating this species by including it in models 6—9 and 12—15 (Table 2) led to its rejection together with the rejection of other species. The inability of the present work and that of some others (Table 4) to detect this may be attributed to the magnitude of the uranium(VI) concentrations involved; however, it should be noted that the contribution of the (2,1) species to these earlier data would be very small and, indeed, the reported values[11] were not always refined simultaneously in these investigations with the other formation constants.

The (2,2) species, $[(UO_2)_2(OH)_2]^{2+}$, a member of all the models in Table 4, and which was first postulated in 1947 by a number of investigators,[23] can be both a major or minor species depending on the pH (Figure 1). The agreement between the values for $-\log \beta_{22}$ in Table 4 (except for the value in sulphate medium[5,10] where complexing by the medium is important) is surprising considering the differences in the various ionic media, and in the models chosen.

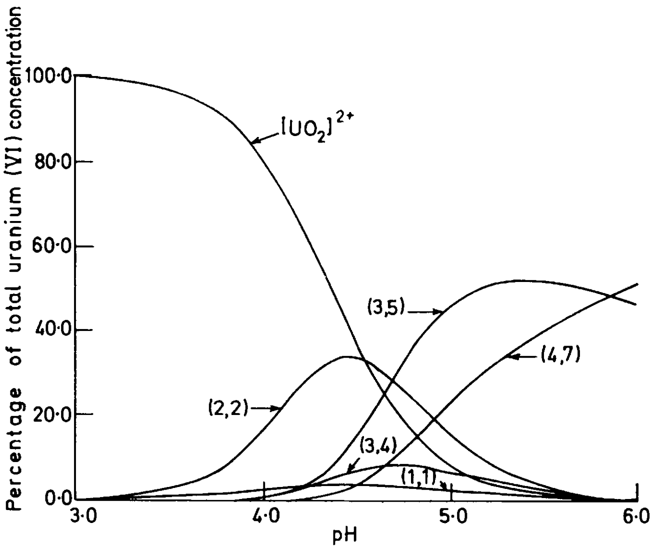

FIGURE 1 Percentage distribution of uranium(VI) in various species, (p,q), for a total concentration of 10^{-3} mol dm^{-3}. For these calculations it is assumed that $[H^+] = 10^{-pH}$, that is $\lambda = 1$

The existence of the core-plus-links trimer, $[(UO_2)_3(OH)_4]^{2+}$, has been considered to depend on the presence of chloride ions,[9,10,17] although no explanation has been offered as to why chloride should preferentially complex this species. In the various media examined by the Sillén School,[9–12] only the data[9] for 3.0 mol dm^{-3} (Na)Cl provided a reasonably certain result; in other instances the (3,4) species was either poorly detected[10,11] (estimated relative standard deviations of β_{34} being $>20\%$) or not detected at all.[12] Similarly, from work originating from Oak Ridge National Laboratory,[6–8] its presence was detected only in 1.0 mol dm^{-3} (Na)Cl. Baes and Mesmer[17] consider that these findings represent a ' very well documented case where the hydrolysis scheme is affected by the medium anions.'

The present results contradict the assertion that the presence of chloride ions is necessary for the (3,4) species to be produced. Although only a minor species, up to *ca.* 8% of the total U^{VI} in a 10^{-3} mol dm^{-3} solution is in this form at pH 4.7 (Figure 1), and its exclusion from model 12 increases the error-square sum (model 14, Table 2) by more than a factor of two. The formation of $[(UO_2)_3(OH)_4]^{2+}$ in chloride media will be the subject of a future investigation.

Figure 1 illustrates that (for 10^{-3} mol dm^{-3} total U^{VI}) the formation of the trimers, the (3,4) and (3,5) species, begins at the same pH value of *ca.* 4.0 but beyond 4.2 the (3,5) species is of much greater importance and becomes the major hydrolysis product in the range pH 4.7—5.8. It is tempting to speculate that the deprotonation of $[(UO_2)_3(OH)_4]^{2+}$ is accompanied by a change from a linear to a clustered structure, thus making the $[(UO_2)_3(OH)_5]^+$ the more stable of the two. Such a structure, for example,[17] a triangle of uranium atoms singly bridged with three hydroxide groups and capped top and bottom with two triply bridging hydroxide groups, seems more likely than an unsymmetrical structure containing a terminal hydroxide, as suggested by Evans.[24] The agreement in the various values of $-\log \beta_{35}$ in Table 4, like that for $-\log \beta_{22}$, is also very good (except, again, for the sulphate medium).

At pH $>$ *ca.* 5 the (4,7) species becomes important. The failure of the data to reflect adequately the (4,6) species perhaps indicates its small importance compared with the deprotonated form. This is consistent with the data obtained for the (3,4) and (3,5) species and, as such, an extension of the data to include more titration points might provide better evidence for the formation of the (4,6) species. However, it should be stressed that when a series of complexes is produced there will always be a poorly defined cut-off point because of the presence of some species in low concentrations. This model error is probably one of the more important sources of systematic errors.

An examination of the different values of $-\log \beta_{pq}$ for each species in the models in Table 2 reveals that least variation occurs in those with the smallest estimated standard deviation. The near constancy of $-\log \beta_{22}$ in models 1, 2, 6, 8, 9, and 12—15 (range 5.83—5.89) is remarkable; this also applies to a lesser extent to the (3,5) species (range 16.26—16.59, in the same models). Thus, the inclusion of relatively minor species in the speciation schemes in general improves the overall goodness of fit and thus decreases model error, the precision of the β_{pq} values of at least the major species remaining almost unchanged. These numerical results may provide a better perspective with which the ' reality ' of any species in a given scheme can be judged.

In precise potentiometric-titration data the greatest sources of error are non-random and consist of model error together with errors in the experimentally observed quantities which result from the experimental design of the normal titration procedure.[25] Thus, estimated standard deviations are of no statistical significance and merely demonstrate the precision of the equilibrium constants produced by the minimisation procedure in the presence of these non-random errors. Therefore, the estimation of errors in the equilibrium constants from the calculated standard deviations is a hazardous and perhaps an erroneous procedure. The error in the constants (that is, the accuracy) cannot be estimated unless all the non-random errors are known and can be accounted for; in practice, this is rarely possible. Thus, we do not believe that meaningful estimates of the accuracy of the reported constants can be made in work of this kind. However, the estimated standard deviations, considered as an index of precision, do allow comparisons between different models and also between the results of different investigations, given comparable model-acceptance criteria.

Sillén and his School must be credited with the establishment of both the experimental techniques and the numerical methods required to investigate complex equilibria in general and hydrolytic equilibria in particular. This pioneering work has, indeed, made the present work possible. However, when comparing the present work with the investigations of this school [5,9-12] (and other investigations [6-8]) certain limitations have to be considered.

The use of very high metal-ion concentrations (up to 1.2 mol dm^{-3}, see Table 4), that is, the partial self-medium method, leads unavoidably to serious uncertainties in the conversion of pH values into hydrogen-ion concentrations as a result of compositional changes occurring during a titration. Thus, irrespective of the precision of the measurements, important systematic errors will be present.[17] This is very important in the uranium(VI) system since the hydrolysis reactions are extensive before precipitation. The results, for example, of Hietanen *et al.*[11] illustrate the effect of this problem in three ways, namely: (*a*) the failure of some of the data to give satisfactory results when they are processed all at once (as the present data are); (*b*) the dependence of some constants on the total uranium(VI) concentrations; and (*c*) imprecision in the $-\log \beta_{pq}$ values of minor species. The total uranium(VI) concentrations used in other investigations of the Sillén and other schools (Table 4) are lower than in the above example and the reported results show a corresponding improvement.

The significance of this problem can also be seen from Figure 2 in which the error-square sum of model 12 is plotted against a range of λ values. The minimum present in Figure 2 ($\lambda = 0.850$) obtained by repeating the calculations for a given λ over the λ range is, as expected, the same as that obtained by allowing λ to be automatically refined. The use of a constant value of λ will require that the total metal-ion concentrations examined be only a small percentage (in the present work, a maximum of *ca.* 2%) of the ionic strength of the medium used so that compositional changes are as small as possible. The value of λ will be important in pH regions beginning at *ca.* 2 units from neutrality; λ is thus important in the present work but not in the case of Cu^{II}.[1]

The discrepancies between the present and earlier work, as far as detected species and the total uranium(VI) concentrations are concerned, can probably be partly explained in terms of compositional changes causing significant systematic errors in pH conversion. Thus, the call (for example [26]) for investigations into hydrolytic equilibria to examine as wide a range as possible of metal-ion concentration must be tempered more by this aspect than by any other. However, comparisons of different investigations, generally, can be difficult and involve, among other things, the complex relations between: (*a*) the total metal concentrations used; (*b*) the experimental pH range and the number of titration points in various sub-ranges; (*c*) the extent of formation of the various species; and (*d*) the proportion of points to which the various species make a measurable contribution. In addition, the criteria used in all the earlier work for accepting a particular model are not given.

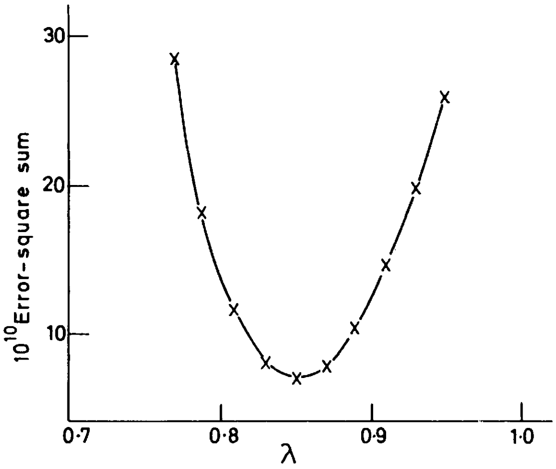

FIGURE 2 The error-square sum of model 12 plotted as a function of λ

Another aspect of this problem is that in some systems the use of high metal-ion concentrations can lead to the simultaneous existence of so many species that, on numerical grounds, the problem of finding the 'best' model becomes exceedingly difficult. On this and the above grounds, it must be concluded that, at least initially, a narrow range of total metal-ion concentration is preferred, the values being as low as practicable. In addition, when there are numerous species, many titration points will be required in this narrow range in order to adequately determine the 'best' model.

Finally, it should be pointed out that for the uranium(VI) system the presence of high concentrations of cations seriously limits the accessible pH range because of the increased ease of precipitation of the 'uranates' which incorporate these cations. Our results in a parallel investigation at a higher ionic strength (1.0 mol dm^{-3} $K[NO_3]$) demonstrate this and, indeed, data treatment in that case is not satisfactory if our criteria are applied. The present results for 0.1 mol dm^{-3} $K[NO_3]$ suggest that the pH range is more important than the range of total metal-ion concentrations.

APPENDIX

The mass-balance equations appropriate to hydrolysed metal-ion systems are (ignoring charges) (A1) and (A2),

$$[T_{\mathrm{M}}]_k = [\mathrm{M}]_k + \Sigma p \beta_{pq}[\mathrm{M}]_k{}^p[\mathrm{H}]_k{}^{-q} \qquad \text{(A1)}$$

$$[T_H]_k = [\mathrm{H}]_k - [\mathrm{OH}]_k - \Sigma q \beta_{pq}[\mathrm{M}]_k{}^p[\mathrm{H}]_k{}^{-q} \qquad \text{(A2)}$$

where $k = 1, \ldots K$ and K is the total number of titration points in all the titrations. Here, $[T_{\mathrm{M}}]_k$ and $[T_{\mathrm{H}}]_k$ refer to total metal concentration and the analytical excess of hydrogen ions, respectively, at a given titration point, and $[\mathrm{M}]_k$, $[\mathrm{H}]_k$, and $[\mathrm{OH}]_k$ are the free concentrations of metal, protons, and hydroxide ions, respectively.

During a titration, when adding base (hydroxide ions) of concentration B, equations (A3) and (A4) are applicable.

$$[T_{\mathrm{M}}]_k = M_0V_0/V \qquad \text{(A3)}$$

$$[T_{\mathrm{H}}]_k = [H_0V_0 - B(V - V_0)]/V \qquad \text{(A4)}$$

Here M_0, H_0, and V_0 are, respectively, the concentrations of total metal and analytical excess of hydrogen ions, and the volume at the beginning of the titration, and V is the volume at a given point in the titration. Each titration yields a different set of parameters (M_0, H_0, V_0, V). It should be noted that here H_0 corresponds to $[H_1]^0$ in Part 1.[1]

As discussed earlier, it is assumed that $[\mathrm{H}]_k = (H_{\mathrm{a}})_k/\lambda$ where $H_{\mathrm{a}} = 10^{-\mathrm{pH}}$ and λ is a correction factor which includes the proton activity coefficient and other contributions (assumed constant) to the pH values (such as the liquid-junction potential and calibration errors). We define $\beta_{pq}{}^* = \beta_{pq}\lambda^q$ and rewrite the mass-balance equations in the forms (A5) and (A6) where [OH] is now given by $10^{-14}/\gamma_{\mathrm{OH}}H_{\mathrm{a}}$.

$$[T_{\mathrm{M}}]_k = [\mathrm{M}]_k + \Sigma p \beta_{pq}{}^*[\mathrm{M}]_k{}^p(H_{\mathrm{a}})_k{}^{-q} \qquad \text{(A5)}$$

$$[T_{\mathrm{H}}]_k = [(H_{\mathrm{a}})_k/\lambda] - [\mathrm{OH}]_k - \Sigma q \beta_{pq}{}^*[\mathrm{M}]_k{}^p(H_{\mathrm{a}})_k{}^{-q} \qquad \text{(A6)}$$

The object is to find values for $[\mathrm{M}]_k$, the $\beta_{pq}{}^*$, λ, and the various H_0 which, when the pH data are being processed, minimise the sum of squares $U = \sum_{i=1}^{2K} R_i{}^2$, where R_i is the residual in a mass-balance equation. The general computer program MINIQUAD 75 is used. However, a complete treatment of the proton mass-balance equation requires introducing a functional relation between pH measurements and hydrogen-ion concentrations and allowing for the initial hydrolysis reactions. These reactions occur to an unknown extent and hence H_0 is a refinable parameter for each titration.[1] Only when the initial extent of hydrolysis is truly negligible can H_0 be set equal to the initial hydrogen-ion concentration. The above special features introduced into the proton mass-balance equation require modification of the program to ensure proper treatment of pH-titration data. In all other respects the program remains quite general.

If N_{t} is the number of titrations, then the number of additional unknowns in the modified program is $N_{\mathrm{t}} + 1$, that is, the N_{t} variables H_0 and $\mu = 1/\lambda$ (we refine for $1/\lambda$ rather than λ to ensure that the proton mass-balance equation has the simpler linear dependence on the unknown). Including these additional parameters does not alter the economy of time or storage achieved by MINIQUAD 75.

MINIQUAD 75 uses a composite iterative least-squares method in which the Gauss–Newton shift vector $\{\boldsymbol{s}_j\}$, relative to the unknown parameters $\{x_j\}$, is given by the solution of equation (A7) where A is a matrix whose

$$A^{\mathrm{T}}A\boldsymbol{s} = -\boldsymbol{g} \qquad \text{(A7)}$$

elements are $A_{ij} = x_j(\partial R_i/\partial x_j)$, and $\boldsymbol{g}$ is a vector whose elements are defined in (A8).

$$g_j = \sum_{i=1}^{2K} x_j(\partial R_i/\partial x_j)R_i \qquad \text{(A8)}$$

If k corresponds to the proton mass-balance equation for any point in a particular titration (H_0 corresponding to some x_j), then $A_{ij} = -H_0V_0/V$ for $i = k$ and 0 for $i \neq k$, and $g_j = -\sum_k (H_0V_0/V)R_k$. For μ corresponding to some x_j, we now let k correspond to the proton mass-balance equation for any point in any titration. Then $A_{ij} = \mu H_{\mathrm{a}}$ for $i = k$ and 0 for $i \neq k$, and $g_j = \sum_k \mu H_{\mathrm{a}}R_k$. Expressions for the other elements of matrix A and vector $\boldsymbol{g}$ remain as before.[20]

Since, for a particular p and q, we have $\beta = \mu^q\beta^*$, the estimated relative standard deviation of β, *i.e.* $[\sigma(\beta)/\beta]$ must be found in terms of the calculated relative standard deviations of μ and β^*, *i.e.* as in equation (A9). Further, the

$$\left[\frac{\sigma(\beta)}{\beta}\right]^2 = \left[\frac{\sigma(\beta^*)}{\beta^*}\right]^2 + q^2\left[\frac{\sigma(\mu)}{\mu}\right]^2 - 2q\frac{\mathrm{cov}(\beta^*,\mu)}{\beta^*\mu} \qquad \text{(A9)}$$

correlation coefficients between the β values can be found by using relation (A10) for the covariance, $\mathrm{cov}(\beta_1,\beta_2)$.

$$\frac{\mathrm{cov}(\beta_1,\beta_2)}{\beta_1\beta_2} = \frac{\mathrm{cov}(\beta_1{}^*,\beta_2{}^*)}{\beta_1{}^*\beta_2{}^*} + q_1q_2\left[\frac{\sigma(\mu)}{\mu}\right]^2 + q_1\frac{\mathrm{cov}(\beta_1{}^*,\mu)}{\beta_1{}^*\mu} + q_2\frac{\mathrm{cov}(\beta_2{}^*,\mu)}{\beta_2{}^*\mu} \qquad \text{(A10)}$$

The following additional points should be noted. (*a*) The initial estimate of H_0 for a titration is taken to be $10^{-\mathrm{pH}}$ at the beginning of the titration. (*b*) The changes in the design matrix A and gradient vector $\boldsymbol{g}$ in MINIQUAD 75 relate to the B cycle.[21] The A cycle, which refines for the free metal independently of the other parameters, remains unchanged except that when the β shifts are repeatedly halved to avoid an increase in the sum of squares the shifts for the additional parameters μ and H_0 are also halved. (*c*) The number of degrees of freedom is reduced by $N_{\mathrm{t}} + 1$. (*d*) The R factor used is given by $[U/\Sigma(T_{\mathrm{M}}{}^2 + T_{\mathrm{B}}{}^2)]^{\frac{1}{2}}$ where $T_{\mathrm{B}} = [B(V - V_0)]/V$ which is the total base concentration added, and the summation is taken over all the titration points.[1] (*e*) Minimisation was not found to be possible when the refinable parameter, μ, appeared explicitly in the species terms; β^* was therefore refined rather than β. In addition, since the parameter μ cannot be sensibly refined when its value is unimportant (as in the case of $\mathrm{Cu^{II}}$), refinement for μ has been made optional. When refined, unity is an acceptable initial estimate of μ.

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