

Spectrophotometric and Potentiometric Study of Uranyl Hydrolysis in Perchlorate Medium.

Is Derivative Spectrophotometry Suitable for Search of the Chemical Model?*

P LUBAL and J. HAVEL**

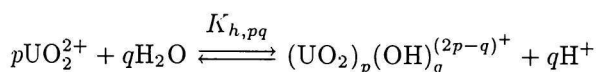
*Department of Analytical Chemistry, Faculty of Science,
Masaryk University, CZ-611 37 Brno*

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Uranyl hydrolysis ($I = 3.00 \text{ mol dm}^{-3} \text{ NaClO}_4$, $T = 298.15 \text{ K}$) was studied by potentiometry and spectrophotometry. Numerical analysis of experimental data yielded the logarithmic values of hydrolytic constants for $(\text{UO}_2)_p(\text{OH})_q^{(2p-q)+}$ species with (p, q) indices: (2, 2) – 6.24 ± 0.02 , (3, 5) – 16.80 ± 0.04 , and (3, 4) – 12.8 ± 0.1 (potentiometry) and (2, 2) – 6.13 ± 0.02 , (3, 5) – 16.81 ± 0.02 , and (3, 4) – 12.57 ± 0.02 (average values obtained by derivative spectrophotometry from the first to the fourth order). The spectra of hydrolytic species were deconvoluted and the use of derivative spectrophotometry in equilibria studies has been discussed.

Uranyl ion is a linear dioxo cation, hydrolyzing at pH values above 2.5 [2–4]. Different polynuclear hydroxo species are formed in the region up the pH value, until precipitation of uranyl hydroxide ($K_s = 10^{-21}$).

The hydrolytic reaction of uranyl can be written



where the equilibrium hydrolytic constant is defined as

$$K_{h,pq} = [(\text{UO}_2)_p(\text{OH})_q^{(2p-q)+}][\text{H}^+]^q[\text{UO}_2^{2+}]^{-p} \quad (1)$$

We will continue in abbreviating hydrolytic species using their indices in the brackets (p, q) .

The hydrolysis was investigated by different authors [2] using a variety of techniques (potentiometry, spectrophotometry, cryoscopy, solubility measurements, extraction, kinetic measurement, chromatography, ultracentrifugation – determination of molecular mass of major species in solution). Also the temperature dependence of hydrolysis and the influence of ionic medium (NaClO_4 , NaCl , KCl , KNO_3 , NaNO_3 , etc.) at different ionic strength (from 0 to 3 mol dm^{-3}) and solvent (light and heavy water, water–ethanol mixture [5], etc.) were determined. In the fifties the “core + links” theory was quite popular [2–4]. There was an effort to explain the acid-base behaviour of

heavy metal ions in solution. The product composition should be member of an infinite series $(1+n, 2n)$. Later the hypothesis was left as there were opposite facts (no possibility to explain the formation of some species). It has been found that uranyl hydrolysis produced species (2, 2) and (3, 5) (major) and (2, 1) and (3, 4) (minor) in all kinds of ionic media [3, 4]. In very diluted alkaline solutions the formation of (1, 1), (1, 2), and (1, 3) species was proved. The stability constants of (4, 6), (4, 7), and (5, 8) species are strongly influenced by ions of the medium because stable ternary complexes are formed [4]. The indication of polymer cluster species in gaseous state by means of fast atom bombardment (FAB) was presented in [6]. The overview of uranyl hydrolytic constants is given in Table 1.

As seen from Table 1, the spectrophotometric method has not been applied yet to study uranyl hydrolysis in 3 M sodium perchlorate [3, 4, 13]. The main task of this work was to determine the spectral properties of hydrolytic species and compare the results with those obtained by potentiometry. In addition, the possibility to use derivative spectrophotometry, outlined briefly in [1], was studied in detail.

EXPERIMENTAL

Uranyl perchlorate was prepared from solid uranyl nitrate by adding slight excess of concentrated per-

*See Ref. [1].

**The author to whom the correspondence should be addressed.

Table 1. Review of Uranyl Hydrolytic Constants at Ionic Strength $I = 3.00 \text{ mol dm}^{-3} \text{ NaClO}_4$

Method	Stoichiometry (p, q)	$\log K_{h,pq}$	Remark, year	Ref.
Potentiometry	(2, 1)	-3.68	1959	
	(2, 2)	-6.31	self method	[7]
	(3, 4)	-12.60		
Potentiometry	(2, 1)	-3.70 (fixed)	1963	
	(2, 2)	-6.04 ± 0.01	model with	
	(3, 4)	$-13.21 (< -12.97)$	(4, 6) species	[8a, b]
	(3, 5)	-16.53 ± 0.01		
	(1, 1)	$-6.10 (< -5.86)$		
Calorimetry	(2, 2)	-6.02	1968	[9a, b]
	(3, 5)	-16.54		
Potentiometry	(2, 2)	-6.17 ± 0.01	1972	[10]
	(3, 4)	-12.92 ± 0.05		
	(3, 5)	-17.04 ± 0.01		
Potentiometry	(2, 2)	-6.0 ± 0.1	1979	[11]
	(3, 5)	-16.6 ± 0.1		
Potentiometry	(2, 2)	-6.13	1982	[4]
	(3, 5)	-16.65	NaNO_3^α	
Potentiometry	(2, 2)	-6.64 ± 0.04 (-6.37)*	1963	[8a, 12]
	(3, 4)	-12.54 ± 0.08 (-14.18)*	NaCl	
	(3, 5)	-18.07 ± 0.11 (-17.19)*		

For another ionic medium only a formula with no other information is given.

* Recalculated according to SIT (specific interaction theory, reference in [4]) from $I = 3.0 \text{ mol dm}^{-3} (\text{NaCl})$ to $I = 3.0 \text{ mol dm}^{-3} (\text{NaClO}_4)$.

α Possible formation of ternary species.

chloric acid ($\varphi = 70 \%$) and evaporating the solution almost to dryness until the reaction for nitrate was negative. The product was recrystallized twice from diluted perchloric acid solution. Then it was dissolved in water, adding slight amount of perchloric acid to prevent hydrolysis. Concentration was determined using Gran transformation [14] of the alkalimetric titration curve. The uranyl content was determined gravimetrically as U_3O_8 (precipitation with H_2O_2) and also by the 8-hydroxyquinoline method [15]. Good agreement of both methods was found.

Sodium perchlorate, anal. grade (Lachema, Brno, Czech Republic) was purified by sodium hydroxide precipitation to remove trace heavy metal ions and the product was recrystallized several times [16].

Carbonate-free sodium hydroxide solution was prepared according to standard technique [16] and it was standardized by hydrazinium sulfate [17] with potentiometric and/or visual end-point indication of the titration.

UV VIS measurements were done on a one-beam diode array spectrophotometer HP 8452A (Hewlett—Packard, USA). The derivative spectra were computed using standard HP 8452A software.

The proton concentration of solutions was checked by a combined Radelkis OP-8080 glass electrode (MOM, Hungary), in which the inner saturated potassium chloride solution was removed from the reference part of the electrode and substituted with 2.99 mol dm^{-3} sodium perchlorate solution and 0.01 mol

dm^{-3} sodium chloride solution, saturated with silver chloride. The reliability of the electrode was tested measuring time stability of the potential. The electrode parameters were determined calibrating the corresponding electrode titrating known amount of perchloric acid by standardized sodium hydroxide solution at given ionic strength medium. Recalculation of $-\log [\text{H}^+]$ values from the measured potential was done by means of equation

$$E = E^0 - g \times \log \{[\text{H}^+]\} + E_j \quad (2)$$

where E^0 is the potential of cell at $-\log [\text{H}^+] = 0$, g is the Nernstian slope given by the term $2.30259(RT/F)$ and E_j is a junction potential. For potentiometric measurements a digital pH-meter Radelkis OP-208 (MOM, Hungary) was used.

All experiments were carried out at ionic strength $I = 3.00 \text{ mol dm}^{-3} \text{ NaClO}_4$ and temperature $(298.2 \pm 0.2) \text{ K}$.

The calculations were done by means of SQUAD [18], LETAGROP SPEFO [19], FA608 [20], POLET [21], and HALTAFALL [22] programs on a PC AT 386.

RESULTS AND DISCUSSION

The absorption spectra are shown in Fig. 1. They demonstrate that by increasing the hydroxide concentration in solution the absorption maxima of uranyl

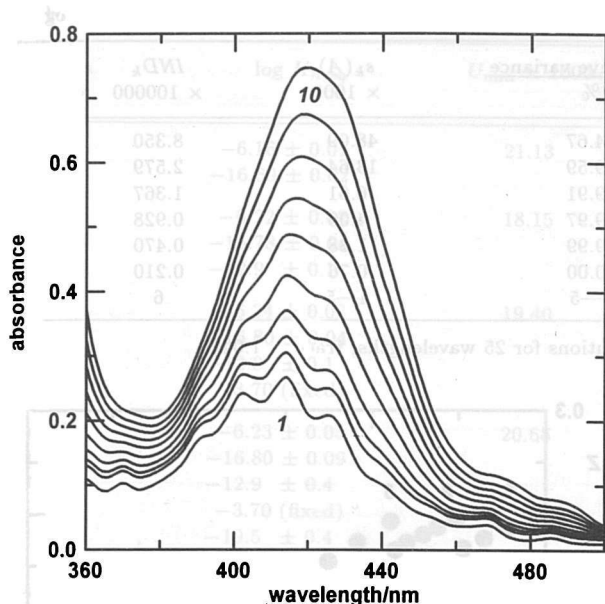


Fig. 1. Absorption spectra for the system uranyl—hydroxide. $c_M = 0.0331 \text{ mol dm}^{-3}$, $-\log \{[H^+]\}$ for: 1. 2.23; 2. 3.03; 3. 3.18; 4. 3.38; 5. 3.47; 6. 3.58; 7. 3.66; 8. 3.73; 9. 3.79; 10. 3.85.

shift towards longer wavelengths. The spectrum with sharp and narrow peaks of the bands changes by increasing the $-\log [H^+]$ values to a spectrum which seems to be only one broad band. It can be assigned to formation of several polynuclear species. This is evident in Fig. 2, which demonstrates the change of molar absorptivity in dependence on uranyl concentrations. The hydrolysis of uranyl starts at the concentration level $8\text{--}33 \text{ mmol dm}^{-3}$ and $-\log [H^+]$ equal to three.

Determination of the Number of Light-Absorbing Species

Generalized form of Bouguer—Lambert—Beer law can be written in matrix notation

$$\mathbf{A} = \mathbf{E}\mathbf{C} \quad (3)$$

where \mathbf{A} is the $n_w \times n_s$ absorbance matrix, \mathbf{E} is the $n_w \times n_c$ matrix of molar absorptivities, \mathbf{C} is the $n_c \times n_s$ concentration matrix. Here n_w denotes the number of wavelengths, n_s means the number of solutions the spectra of which have been recorded, and n_c is the number of components which absorb in the chosen spectral range. The rank of the matrix, $\text{rank}(\mathbf{A})$ (RM) is obtained from the equation

$$\text{rank}(\mathbf{A}) = \min(\text{rank}(\mathbf{E}), \text{rank}(\mathbf{C})) \leq \min(n_w, n_c, n_s) \quad (4)$$

Since the $\text{rank}(\mathbf{A})$ is equal to the rank of \mathbf{E} or \mathbf{C} , whichever is the smaller, and since $\text{rank}(\mathbf{E}) \leq n_c$ and $\text{rank}(\mathbf{C}) \leq n_c$, then provided that n_w and n_s equal to or are greater than n_c , it will only be necessary to

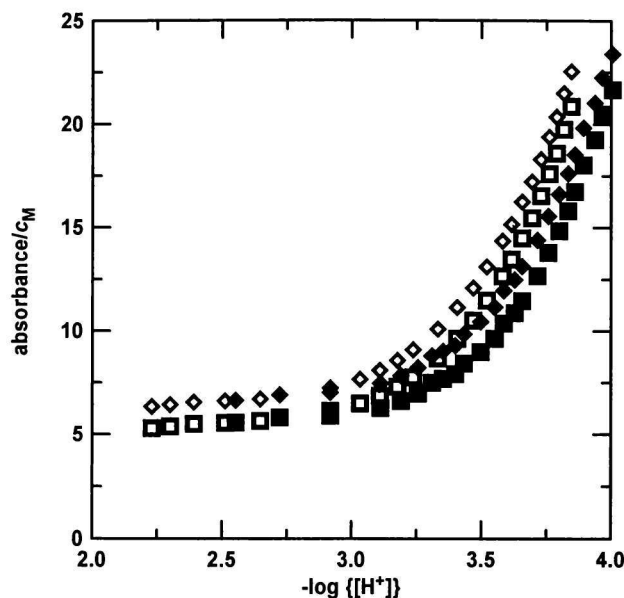


Fig. 2. Absorbance curves for the uranyl—hydroxide system. \square, \diamond $c_M = 0.0331 \text{ mol dm}^{-3}$ and $\blacksquare, \blacklozenge$ $c_M = 0.0083 \text{ mol dm}^{-3}$; \diamond, \blacklozenge $\lambda = 420 \text{ nm}$ and \square, \blacksquare $\lambda = 430 \text{ nm}$.

determine the rank of \mathbf{A} and find the number of absorbing species. We assume that the $\text{rank}(\mathbf{A})$ is equal to the number of linearly independent columns of \mathbf{A} , expressed as the number of non-zero eigenvectors (it means that the concentration of one or more species cannot be expressed as a linear combination of other species in all experiments).

For calculation of RM the Simmonds—Wernimont—Kankare method [20] was applied. The second moment matrix given by formula

$$\mathbf{M} = \frac{1}{n_s} \mathbf{A}\mathbf{A}^T \quad (5)$$

is a symmetric (square) matrix of order n_s and of rank n_c , $\text{rank}(\mathbf{M}) \leq n_c$. Each element of the absorbance matrix \mathbf{A} is a subject to experimental error and because of that fact, the number of non-zero eigenvalues is $\min(n_w, n_s)$. Let the eigenvalues of \mathbf{M} be EV_i , matrix trace of \mathbf{M} $\text{tr}(\mathbf{M})$, and suppose that there are k independent components in the system. Then the residual standard deviation of absorbance is given by

$$s_k(A) = \frac{\text{tr}(\mathbf{M}) - \sum_{i=1}^k EV_i}{\sqrt{n_w - k}} \quad (6)$$

relative variance

$$RV(\%) = \frac{EV_i}{\text{tr}(\mathbf{M})} \times 100 \quad (7)$$

cumulative relative variance

$$CRV(\%) = \frac{\sum_{i=1}^k EV_i}{\text{tr}(\mathbf{M})} \times 100 \quad (8)$$

Table 2. Results of Factor Analysis of Spectrophotometric Data of the System Uranyl—Hydroxide Calculated by FA608 Program

k	Eigenvalue $\times 100$	Variance %	Cumulative variance %	$s_k(A)$ $\times 1000$	IND_k $\times 100000$
1	98.95	94.67	94.67	48.09	8.350
2	5.12	4.91	99.59	13.64	2.579
3	0.33	0.32	99.91	6.61	1.367
4	0.06	0.06	99.97	4.09	0.928
5	0.03	0.03	99.99	1.88	0.470
6	0.01	0.01	100.00	0.76	0.210
RM		4—5	4—5	4—5	6

Uranyl concentration 8.3, 16.6, and 33.1 mmol dm⁻³, data set 48 solutions for 25 wavelengths, τ_{av} 1.0425.

and Malinowski's indicator function IND_k by Malinowski [23]

$$IND_k = \frac{s_k(A)}{(n_w - k)^2} \quad (9)$$

Let the precision of the absorbance measurement be given by the standard deviation of absorbance of spectrophotometer used $s_{\text{inst}}(A)$. Then we may say that if $s_k < s_{\text{inst}}(A)$, it is probable that $n_c < k$ and Malinowski's indicator function number shows minimum value [23].

The rank of the absorbance matrix enables to predict the number of light-absorbing species in solution. The number of complexes formed was estimated from the first step of factor analysis of absorption matrix PCA (principal component analysis) (Table 2). It follows from this analysis that there are 4—5 absorbing species formed, which is indicated by relative variance, cumulative relative variance, and abundance standard deviation. Malinowski's indicator function IND_k gives unreliably high number of the components [24]. This criterion should be considered unreliable [25] in most cases. From low contribution of relative variance to the trace of the second moment absorbance matrix we can conclude that there are three species in the solutions, except that of uranyl, with different spectral properties.

The Search of Chemical Model

The facts described above were used for deduction of a chemical model from potentiometric data. The data were transformed to Z function given by the relationship [11]

$$Z = \frac{c_{\text{H}^+} + [\text{OH}^-] - [\text{H}^+]}{c_{\text{UO}_2^{2+}}} \quad (10)$$

The graphical plot of this function as $-\log [\text{H}^+]$ dependence of different uranyl concentrations is shown in Fig. 3. These data were used for calculation of hydrolytic constants for each species, using the condition of a residual function

$$U = \sum_{i=1}^N (Z_{\text{exp},i} - Z_{\text{calc},i})^2 \rightarrow \min \quad (11)$$

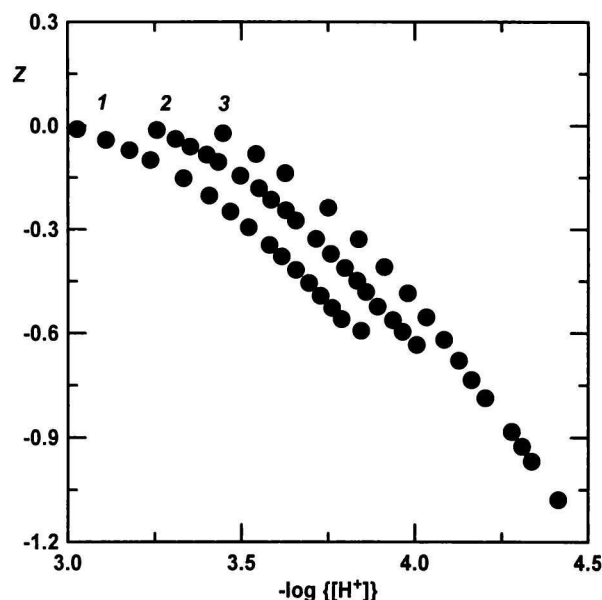


Fig. 3. The formation curves for the uranyl—hydroxide system. c_M : 1. 0.0331 mol dm⁻³; 2. 0.0167 mol dm⁻³; 3. 0.0083 mol dm⁻³

where Z_{exp} are experimental and Z_{calc} calculated values of the formation curve and the summation is done over all N experimental points. The standard deviation of Z function is defined for n calculated parameters as

$$s(Z) = \sqrt{\frac{U}{(N - n)}} \quad (12)$$

We have tested all chemical models described in the literature and the results are given in Table 3. The model with species (2, 2), (3, 5), and (3, 4) seems to be the most probable one (PCA enables to estimate three and/or four absorbing species in solution, except that of uranyl). The values of hydrolytic constants are in a good accordance with the literature data (Tables 1 and 3). This model was tested also by nonheuristic approach. The calculated hydrolytic constants were the same and the minimum was reached during searching of these parameters. The model with (4, 6) species was also tested but the calculation had to be rejected as there was no convergence during the minimization

Table 3. Results of Calculation of Uranyl Hydrolytic Constants from Potentiometric Data Calculated by POLET Program

Species (<i>p</i> , <i>q</i>)	log $K_{h,pq}$	$U_{\min} \times 1000$	$s(Z) \times 1000$	χ^2	R
(2, 2)	-6.16 ± 0.01	21.13	20.93	10.65	0.0435
(3, 5)	-16.69 ± 0.02				
(2, 2)	-6.22 ± 0.02	18.15	18.86	10.02	0.0403
(3, 5)	-16.78 ± 0.04				
(3, 4)	-12.9 ± 0.1				
(2, 2)	-6.24 ± 0.02	19.40	19.50	11.27	0.0416
(3, 5)	-16.80 ± 0.04				
(3, 4)	-12.8 ± 0.1				
(2, 1)	-3.70 (fixed)				
(2, 2)	-6.23 ± 0.05	20.68	20.14	10.65	0.0435
(3, 5)	-16.80 ± 0.09				
(3, 4)	-12.9 ± 0.4				
(2, 1)	-3.70 (fixed)				
(4, 6)	-19.5 ± 0.4				

Data set 51 solutions, uranyl concentration 8.28, 16.6, and 33.1 mmol dm⁻³

process. It is logical because there are some doubts about its existence. The statistical parameters of the quality of the fit were calculated according to the relationship for the Hamilton R factor

$$R = \frac{\sum_{i=1}^N w_i (y_{\text{exp},i} - y_{\text{calc},i})^2}{\sqrt{\sum_{i=1}^N w_i y_{\text{exp},i}^2}} \quad (13)$$

where y is any dependent value.

This value is compared with the limiting value R_{lim} , determined from pessimistic estimates of the errors in all experimental quantities using error-propagation rules and testing the hypothesis. In ideal case this value could reach zero.

We used the Pearson test of the quality of the fit, χ^2 , in which all residuals, *e.g.* differences $y_{\text{exp}} - y_{\text{calc}}$, are divided into eight classes the ranges of which are given by characteristic properties of the Gaussian error distribution. If this distribution of residuals is valid then the probability of abundance in each class is equal to 12.5 %.

We tested also different chemical models for spectrophotometric data using minimization of residual function

$$U = \sum_{i=1}^{n_s \times n_w} (A_{\text{exp},i} - A_{\text{calc},i})^2 \rightarrow \min \quad (14)$$

where A_{exp} are experimental and A_{calc} calculated values of absorbance and the summation is done over all experimental points, *i.e.* number of solutions (n_s) times number of wavelengths (n_w). The standard deviation of absorbance is defined as

$$s(A) = \sqrt{\frac{U}{(n_s \times n_w - n)}} \quad (15)$$

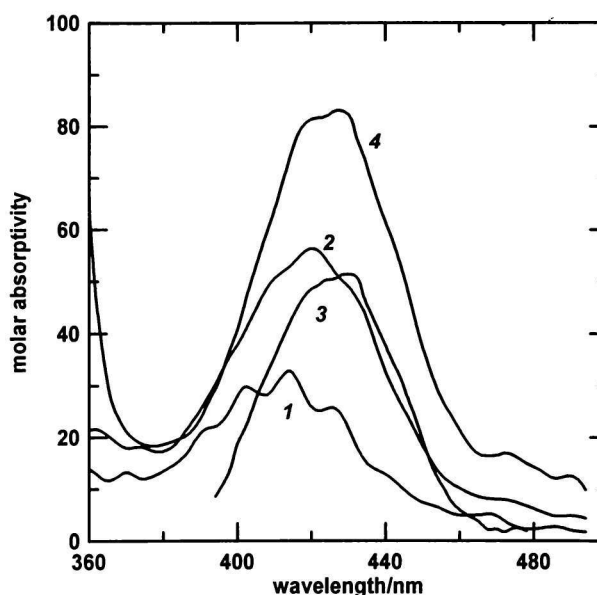


Fig. 4. The calculated molar absorptivities of species in the uranyl—hydroxide system (uranyl molar absorptivity profile was multiplied four times and molar absorptivity profile of the (3, 5) species was divided by four). 1. UO_2^{2+} ; 2. $(\text{UO}_2)_2(\text{OH})_2^{2+}$; 3. $(\text{UO}_2)_3(\text{OH})_4^{2+}$; 4. $(\text{UO}_2)_3(\text{OH})_5^+$

Shooting as initial estimation hydrolytic constants calculated from potentiometric data, no good fit with reliable constants is obtained from spectrophotometric data (Table 4). Using other calculation algorithm (pit mapping in LETAGROP SPEFO [26]), we get the same bad results.

An alternative calculation is based on using derivative spectra (Table 4). Thus, it was possible to determine the chemical model and calculate the molar absorptivity values for each species from weighted

Table 4. Results of the Equilibrium Data Analysis of the Uranyl—Hydroxide System from Spectrophotometric Data by SQUAD Program

Part A				
Spectrum order	$\log K_{h,22}$	$\log K_{h,35}$	$s(A) \times 100000$	
0th derivative	-5.87 ± 0.01	-16.30 ± 0.03	337	
1st derivative	-6.04 ± 0.01	-16.54 ± 0.02	15.46	
2nd derivative	-6.11 ± 0.02	-16.63 ± 0.02	3.00	
3rd derivative	-6.13 ± 0.01	-16.65 ± 0.02	0.37	
4th derivative	-6.12 ± 0.01	-16.65 ± 0.01	0.10	
Weighted average value	-6.098 ± 0.006	-16.62 ± 0.01		
Part B				
Spectrum order	$\log K_{h,22}$	$\log K_{h,35}$	$\log K_{h,34}$	$s(A) \times 100000$
0th derivative	-5.2 ± 0.1	-15.7 ± 0.1	-11.6 ± 0.1	312
1st derivative	-6.04 ± 0.04	-16.66 ± 0.04	-12.64 ± 0.06	14.76
2nd derivative	-6.16 ± 0.05	-16.86 ± 0.05	-12.57 ± 0.04	2.81
3rd derivative	-6.15 ± 0.03	-16.85 ± 0.04	-12.57 ± 0.04	0.35
4th derivative	-6.20 ± 0.03	-16.99 ± 0.05	-12.52 ± 0.04	0.09
Weighted average value	-6.13 ± 0.02	-16.81 ± 0.02	-12.57 ± 0.02	

Data set 21 solutions for 50 wavelengths.

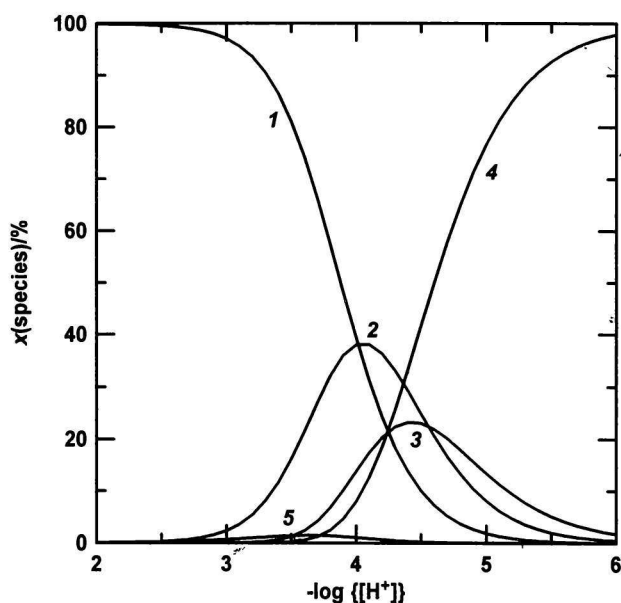


Fig. 5. The distribution diagram in the uranyl—hydroxide system. $c_M = 0.0167 \text{ mol dm}^{-3}$ 1. UO_2^{2+} ; 2. $(\text{UO}_2)_2(\text{OH})_2^{2+}$; 3. $(\text{UO}_2)_3(\text{OH})_4^{2+}$ 4. $(\text{UO}_2)_3(\text{OH})_5^{+}$; 5. $(\text{UO}_2)_2(\text{OH})_3^{3+}$

average hydrolytic constants values of the hydrolytic species (Fig. 4). The distribution diagram is shown in Fig. 5. The molar absorptivity values of hydrolytic species are almost the same as those obtained from connected potentiometric and spectrophotometric data (hydrolytic constant values of each hydroxo

species were fixed and their molar absorptivity values were calculated).

This improvement of the fit for spectrophotometric data has several reasons. We can write combining mass balance with respective hydrolytic constants and Bouguer—Lambert—Beer law equation

$$A_{i,j} = \sum_{k=1}^n \varepsilon_{i,pq} K_{h,pq} [\text{UO}_2^{2+}]^p [\text{H}^+]^{-q} \quad (16)$$

for $i = 1, \dots, n_w$ — number of chosen wavelengths in measured spectra, $j = 1, \dots, n_s$ — c_M , or $-\log [\text{H}^+]$ is changed, $k = 1, \dots, n$ — number of hydrolytic complexes.

If we differentiate over wavelength values n -times, we obtain

$$\frac{\partial^n A_{i,j}}{\partial \lambda^n} = \sum_{k=1}^n \frac{\partial^n \varepsilon_{i,pq}}{\partial \lambda^n} K_{h,pq} [\text{UO}_2^{2+}]^p [\text{H}^+]^{-q} \quad (17)$$

Choosing the wavelength values in the region where the position of the wavelength is under condition $\partial^n A_{i,j} / \partial \lambda^n = 0$, and changing proton and/or metal concentration, we get overdetermined system of equations in order to eliminate “background” efficiently. This determination of the chemical model is more certain. At the same time the respective contribution of individual species to the total signal is higher for values obtained from derivative spectrophotometry than from normal one. The first fact is already known from works concerning analytical determination of several components in a mixture [27]. Secondly, the signal to noise ratio is increasing with contemporaneous smoothing data [28]. Both factors play a very important role.

Table 5. Deconvolution of Calculated Molar Absorptivities into Bands of Gaussian Profile

Species (<i>p</i> , <i>q</i>)	Band parameters	Band number			Squared correlation coefficient	Standard deviation
		1	2	3		
(1, 0)	$\varepsilon_{\max,i}$	2.6 ± 0.2	7.6 ± 0.1	0.9 ± 0.1	0.9882	0.251
	$\lambda_{\max,i}$	360 (fixed)	410.5 ± 0.4	470 ± 4		
	σ_i	25 ± 4	52 ± 2	40 ± 10		
	f_i	4.6×10^{-5}	2.2×10^{-4}	1.5×10^{-5}		
(2, 2)	$\varepsilon_{\max,i}$	25.2 ± 0.8	55.6 ± 0.2	6.1 ± 0.3	0.9987	0.621
	$\lambda_{\max,i}$	345 (fixed)	419.3 ± 0.2	479 ± 1		
	σ_i	60 ± 3	48.1 ± 0.6	32 ± 3		
	f_i		1.4×10^{-3}	7.9×10^{-5}		
(3, 4)	$\varepsilon_{\max,i}$		52.4 ± 0.6		0.9915	1.809
	$\lambda_{\max,i}$		426.0 ± 0.3			
	σ_i		40.2 ± 0.6			
	f_i		1.1×10^{-3}			
(3, 5)	$\varepsilon_{\max,i}$	430 ± 30	330 ± 3	52 ± 5	0.9912	9.369
	$\lambda_{\max,i}$	345 (fixed)	424.1 ± 0.3	482 ± 2		
	σ_i	31 ± 1	49.5 ± 0.8	30 ± 5		
	f_i		4.6×10^{-2}	1.1×10^{-3}		

Fixed values are obtained from logarithmic analysis of the spectrum [29].

Deconvolution of the Spectra of Species

The calculated spectra for each species were deconvoluted into one broad and two narrow bands of Gaussian profile [29] (not only in the case of species (3, 4)

$$\varepsilon_i = \varepsilon_{\max,i} \exp \left[-5.545 \frac{(\lambda - \lambda_{\max,i})^2}{2\sigma_i^2} \right] \quad (18)$$

where ε is the calculated molar absorptivity, ε_{\max} the maximal molar absorptivity at wavelength of the band peak, λ the wavelength, λ_{\max} the wavelength of the band peak, σ the half-width of the absorption band.

The area of spectral band is given by relationship [30, 31] for the so-called oscillator strength

$$f_i = 1000 \ln(10) \frac{mc^2}{\Pi e^2 N_A} \int_{\nu_1}^{\nu_2} \varepsilon d\nu = 4.315 \times 10^{-9} \int \varepsilon d\nu \quad (19)$$

where m and e is charge and mass of electron, respectively, c is velocity of light in vacuum, N_A is Avogadro's number. We get after a simplification [30, 31]

$$f_i \approx 4.60 \times 10^{-9} \varepsilon_{\max,i} \nu_{1/2} \quad (20)$$

if the band has a Gaussian shape with the width in half-height $\nu_{1/2}$. The new relationship (21) after rearrangement for wavelength values in nanometers is identical with relationship (20)

$$f_i \approx 4.60 \times 10^{-2} \varepsilon_{\max,i} \left(\frac{1}{\lambda_{\max,i} - \sigma_i} - \frac{1}{\lambda_{\max,i} + \sigma_i} \right) \quad (21)$$

This value is proportional to probability P of light absorption as quadrate of the so-called transition moment defined by relationships [30]

$$P = \langle \psi_a | M | \psi_b \rangle = e\sqrt{D} \quad (22)$$

where D is the so-called dipole strength of electron transition between states defined by wave functions ψ_a and ψ_b treated by means of the dipole moment operator M . These relationships connect experimental chemistry with theoretical quantum chemistry.

Also deconvolution into bands of Studentian or Lorentzian profile [29] was done, but the Gaussian profile gave the best fit (Table 5). The calculated parameters enable to determine spectral characteristics (eqn (21)). The reciprocal wavelength values in band maximum are proportional to energy levels of electrons in the given species. The energy levels are lower than the respective levels in uranyl ion. The results are comparable with those in Ref. [32] where the authors deconvoluted 24 (14 in VIS region and 10 in UV region) Gaussian profile bands for the uranyl spectra which represent the three main bands in VIS region [2, 32a]. The oscillator strength values for uranyl were estimated for those three bands (Table 5) and compared with the literature data [2, 32a, c]. There is an agreement. We did not observe any considerable shifts in band maxima of hydrolytic species, only increasing intensities and half-widths (Table 5). These phenomena have already been observed [32b]. The structures and intensities of the bands in spectrum are influenced mainly by geometry of the ligands coordinated to the uranyl moiety [33]. In our case, it can be concluded that (2, 2) and (3, 4) species with one or two $\langle(\text{OH})_2\rangle$

bridges are formed by "linear" condensation, while (3, 5) species because of much higher molar absorptivity has a nonlinear structure due to the different condensation process. Thus, $(\text{UO}_2)_3(\text{OH})_5^+$ species should be written $[(\text{UO}_2)\text{O}(\text{OH})_3(\text{H}_2\text{O})_n]^+$ similarly as was proved by X-ray diffraction analysis in solid state [34]. This structure in solution was verified independently using UV VIS spectroscopy.

The molar absorptivity values for (2, 2) and (3, 4) species and also the distribution diagram (Fig. 5) show why it was difficult to determine the hydrolytic constants by normal spectroscopy. These species are formed in the same hydroxide concentration region and, furthermore, they have similar spectral properties (Table 5). Derivative spectroscopy enables better distinguishing of the contributions of each species and, hence, it can be applied with advantage to solve such chemical equilibria problems, where the chemical model is not *a priori* well known.

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