Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Complexation of Uranyl with Benzoic Acid in Aqueous Solution at Variable Temperatures: Potentiometry, Spectrophotometry and DFT Calculations†

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Data processing with Hyperquad and HypSpec programs

Hyperquad can be used to derive equilibrium constants from potentiometric data. HypSpec is a program in the Hyperquad suite and shares some features with other programs in the suite. HypSpec can be used to derive equilibrium constants from spectrophotometric data. (P. Gans et al., Annali di chimica, 1999, 89, 45-49; Talanta, 1996, 43, 1739-1753)

To process the potentiometric or spectrophotometric data, we first edited the format of data according to the requirement of the program and then input them into the program as "titration" data. All known experimental conditions are also required to input along with the titration data (potentials or absorbances). Then, starting speciation models should be given and analyzed by factor analysis to estimate the number of species. With reasonable models, the data are further analyzed and fitted by the program. Reliable fitting is achieved only when the regression is converged and the output is scientifically reasonable (for example, no species with obvious negative absorptions should be generated in spectrophotometric data processing).

In general, the use of the algorithm for computing equilibrium constants in HypSpec and Hyperquad involves the following sequence:

1. Start with a set of known and estimated overall protonation or stability constants (β).
2. Compute the objective function (sum of squares, U) as in Eq. (1)

$$U = \sum_{i\,=\,1,np} W_i r_i^2 \tag{1}$$

where W is a weight and r is a residual, equal to the difference between the observed and calculated values.

3. Change the unknown protonation or stability constants and repeat the calculations until no further reduction of U (i.e., the sigma in HypSpec output, has been minimized) can be obtained.

$$\sigma = (U/np - n)^{1/2} \tag{2}$$

where $np-n$, the number of data points minus the number of parameters is the expectation value of the objective function.

When systematic errors are present, the weighted sum of squares will be more than $np-n$. Good experimental practice seeks to reduce systematic errors to a level where they are small compared with random errors. HypSpec has a facility for calculating the weights based on estimates of the experimental errors. When σ is close to 1 it can be said that the data has been fitted within experimental error.

4. At the end, providing the final calculated logβ values with standard deviation can be accepted as the final results.

For the equations used in the two programs to fit the data, we summarize the following through the literature:

(1) The objective function is given in matrix notation simply as

$$U = r^T W r \tag{3}$$

where r is a vector of residuals, r = ($y^{observed}$ - $y^{calculated}$), $y^{observed}$ represents a measurment in mV, pH or absorbance and W is a matrix of weights.

(2) To minimize the objective function, we use the Gauss-NewtonMarquardt method summarized by the system of normal equations

$$(J^T W J + \lambda D)\Delta p = J^T W r \tag{4}$$

where J is the Jacobian matrix and Δp is a vector of shifts to be applied to the parameters. D is taken as equal to the diagonal elements of $J^T W J$ and λ is the Marquardt parameter which may be zero.

(3) The elements of the Jacobian relative to any unknown parameter p are obtained from the defining equations, the modified Nernst law (ionic charges are omitted for simplicity of notation):

$$E = E^0 + fRT\ln [H]/nF \tag{5}$$

$$\frac{\partial E}{\partial p} = \frac{\partial E}{\partial [H]} \frac{\partial [H]}{\partial p} \tag{6}$$

(4) The Beer-Lambert law:

$$A_\lambda = l \sum_{j=1,na} \varepsilon_{\lambda j} c_j \tag{7}$$

$$\frac{\partial A_\lambda}{\partial x} = l \sum_j \varepsilon_{\lambda j} \frac{\partial c_j}{\partial x} \tag{8}$$

These are solved by the Newton-Raphson method and the normal equations matrix is used to derive $\partial[H]/\partial\beta_k$, $\partial E/\partial n$, $\partial E/\partial E^0$ and $\partial E/\partial a$.

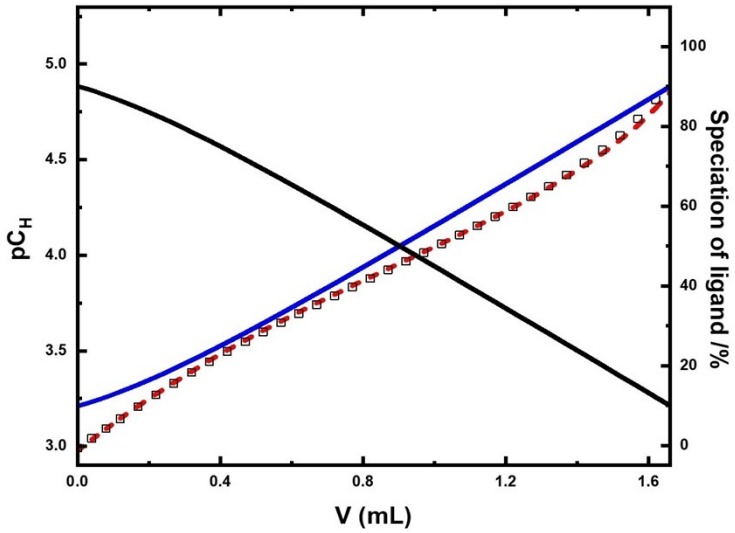

Figure S1. The titration experiment of the protonation constant of benzoic acid. Left y-axis: pC_H, (□) experimental, (---) fitted; right y-axis: Speciation of benzoic acid, (black) benzoic, (blue) benzoate.

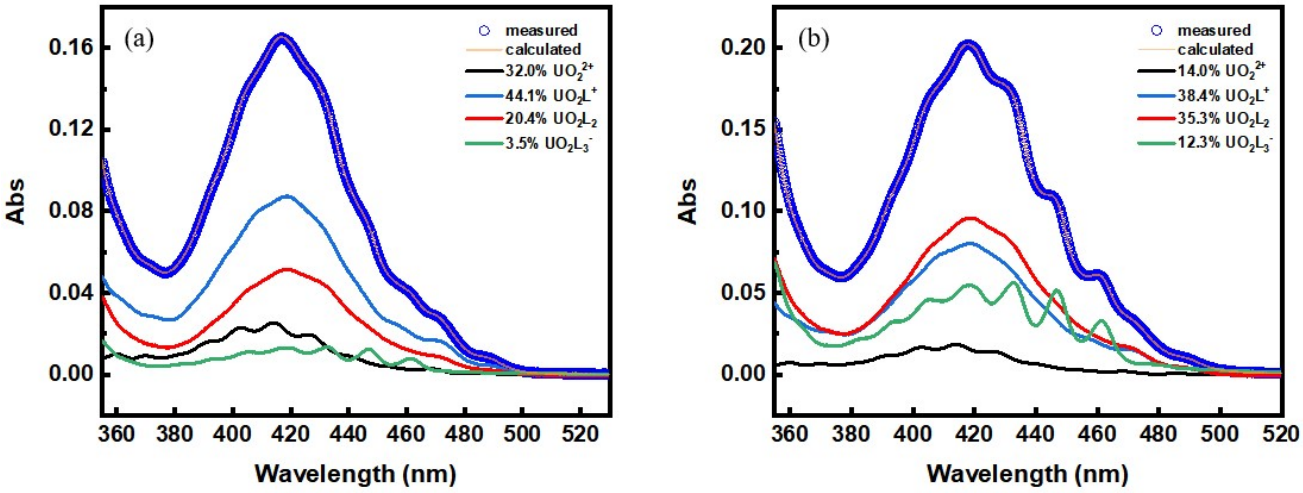

Figure S2. The deconvolution of absorption spectra at two representative conditions. a) $[UO_2^{2+}]$ = 10 mmol/L, [L] = 267.0 mmol/L, I = 0.1 mol/L, pH = 3.7; b) $[UO_2^{2+}]$ = 10 mmol/L, [L] = 267.0 mmol/L, I = 0.1 mol/L, pH = 4.0.

Table S1 Experimental conditions

Exptl[a]	Titr. No.	T K	Titrand (mM/L) C_U^0	C_L^0	C_H^0	$V_{titrand}$ mL	Titrant (mol/L) C_L	$C_{H/OH}$[b]	$V_{titrant}$ mL
Pot	1	298	0.550	14.50	14.95	20.0	0.00	-0.100	2.5
	2	298	0.580	14.50	15.00	20.0	0.00	-0.100	2.5
	3	298	0.580	15.50	14.95	20.0	0.00	-0.100	2.5
	4	313	0.550	12.42	14.90	24.0	0.00	-0.100	2.8
	5	313	0.580	13.00	15.05	24.0	0.00	-0.100	2.8
	6	313	0.580	12.42	14.90	24.0	0.00	-0.100	2.8
	7	328	0.550	11.54	14.00	24.0	0.00	-0.100	2.0
	8	328	0.580	12.50	14.50	24.0	0.00	-0.100	2.0
	9	328	0.580	11.54	14.00	24.0	0.00	-0.100	2.0
	10	343	0.550	12.45	15.38	24.0	0.00	-0.100	2.3
	11	343	0.580	12.00	15.20	24.0	0.00	-0.100	2.3
	12	343	0.580	12.45	15.38	24.0	0.00	-0.100	2.3
Spc	1	298	10.00	0.00	12.00	1.60	0.267	$3.72 \cdot 10^{-3}$	0.24
	2	298	9.05	0.00	12.00	1.60	0.267	$3.72 \cdot 10^{-3}$	0.20
	3	298	12.00	0.00	12.00	1.60	0.267	$3.72 \cdot 10^{-3}$	0.30

[a] Pot – potentiometry; Spc-spectrophotometry

[b] Positive values are for the concentration of proton, and negative values for the concentration of NaOH

Table S2 Hydrolysis constants of U(VI) at different temperatures.

Reaction	T K	$\log\beta^0$[a]	$\log\beta_M$[a] (0.1mol·dm^{-3} $(C_2H_5)_4NClO_4$)	$\log\beta_M$ (0.1 mol·dm^{-3} $NaClO_4$)
$UO_2^{2+}+H_2O=UO_2OH^++H^+$	298	-5.40 ± 0.24	-5.58 ± 0.24	-5.58 ± 0.24
	313	-4.92 ± 0.12	-5.11 ± 0.11	-5.11 ± 0.11
	328	-4.88 ± 0.24	-5.07 ± 0.24	-5.07 ± 0.24
	343	-4.31 ± 0.12	-4.51 ± 0.11	-4.51 ± 0.11
$2UO_2^{2+}+2H_2O=(UO_2)_2(OH)_2^{2+}+2H^+$	298	-5.62 ± 0.04	-5.83 ± 0.02	-5.83 ± 0.02
	313	-5.21 ± 0.03	-5.43 ± 0.01	-5.43 ± 0.01
	328	-4.84 ± 0.05	-5.06 ± 0.03	-5.06 ± 0.03
	343	-4.50 ± 0.05	-4.73 ± 0.03	-4.73 ± 0.03
$3UO_2^{2+}+5H_2O=(UO_2)_3(OH)_5^++5H^+$	298	-15.74 ± 0.05	-16.37 ± 0.02	-16.37 ± 0.02
	313	-14.70 ± 0.04	-15.35 ± 0.01	-15.35 ± 0.01
	328	-13.78 ± 0.05	-14.45 ± 0.02	-14.45 ± 0.02
	343	-12.92 ± 0.05	-13.61 ± 0.02	-13.61 ± 0.02

[a]The values of $\log\beta^0$ and $\log\beta_M$ at I = 0.1 mol·dm^{-3} $(C_2H_5)_4NClO_4$ are from the literature 22.

The coordinates of optimized structures of uranyl complexes by DFT method

Table S3 $[UO_2L(3H_2O)]^+$

U	-1.09172200	0.77855300	0.07293200
O	0.49221000	0.08009100	-0.32387600
O	-1.38277200	-0.94117900	1.89863200
O	-0.01251100	1.83073600	2.09987000
O	-2.62820500	1.51640800	0.56812800
O	-0.46335800	3.04358100	-0.82724300
H	-0.64559400	1.83923200	2.84113400
H	0.71998200	1.26286800	2.40207200
H	0.49696300	3.18946200	-0.74528100
H	-0.87432500	3.74490200	-0.28964200
H	-1.70632900	-0.50350100	2.70719700
H	-0.50995800	-1.30122100	2.14085600
C	-4.15131700	-0.89762100	-5.45588600
C	-4.74772900	-2.15104500	-5.28411400
C	-4.57316700	-2.85598000	-4.08880000
C	-3.80524400	-2.30830100	-3.06323900
C	-3.20653300	-1.05003900	-3.23195600
C	-3.38110900	-0.34645800	-4.43364300
C	-2.40956000	-0.45665400	-2.13261700
O	-1.85323700	0.68992900	-2.26316300
O	-2.27799300	-1.06797100	-1.01401600
H	-4.28932000	-0.35135500	-6.38426500

H	-5.34975800	-2.57802000	-6.08130000
H	-5.03722800	-3.82894100	-3.95679600
H	-3.66774100	-2.84659500	-2.13139800
H	-2.91748800	0.62665000	-4.55726500

Table S4 [$UL_2(H_2O)$]

U	-0.89291200	1.00757200	-0.20841100
O	0.61533000	0.49131400	-1.00640700
O	-2.38816500	1.56136900	0.58937700
O	-0.18262900	3.40765100	-0.45054200
H	0.78873000	3.48583700	-0.43875100
H	-0.49060500	3.94160700	0.30442000
C	-4.48017800	-0.98805000	-5.29326600
C	-4.95615100	-2.28129000	-5.05446000
C	-4.61256000	-2.95083600	-3.87555800
C	-3.79263900	-2.32999500	-2.93500700
C	-3.31661100	-1.03101500	-3.16985800
C	-3.66406200	-0.36158600	-4.35334700
C	-2.45788700	-0.36050100	-2.16280300
O	-2.08779600	0.85647100	-2.32977200
O	-2.08121600	-0.97145600	-1.10531700
H	-4.74644800	-0.46947300	-6.20963100
H	-5.59539900	-2.76682500	-5.78653000
H	-4.98458500	-3.95425300	-3.69059300

H	-3.52252900	-2.84194300	-2.01731600
H	-3.29307200	0.64257900	-4.52961700
C	1.66014100	0.06084700	5.75419600
C	1.25338400	-1.19110100	6.22674200
C	0.46655400	-2.02395700	5.42469900
C	0.08649700	-1.60744700	4.15024500
C	0.48916900	-0.35000400	3.67469800
C	1.27772900	0.48359600	4.48244100
C	0.06765000	0.10273700	2.32555700
O	0.34129900	1.28375600	1.91505700
O	-0.59353000	-0.67499300	1.55304100
H	2.27240300	0.70591000	6.37748600
H	1.54866000	-1.51710400	7.22015000
H	0.14908300	-2.99483700	5.79361800
H	-0.52544100	-2.24649200	3.52236200
H	1.58666100	1.45455000	4.10966600

Table S5 $(UL_3)^-$

U	-1.16919100	1.32926700	-0.08489200
O	0.35256100	0.83181600	-0.88638300
O	-2.69067400	1.82121100	0.72049900
C	-4.66321900	-1.13828100	-5.10540300
C	-4.93756700	-2.48765600	-4.86088300
C	-4.48554500	-3.09419800	-3.68460000

C	-3.75933200	-2.35383800	-2.75308500
C	-3.48209100	-0.99987800	-2.99460400
C	-3.93799000	-0.39495400	-4.17557900
C	-2.70478400	-0.20723900	-2.00344000
O	-2.45872700	1.02818200	-2.21070800
O	-2.27077500	-0.75161100	-0.93262500
H	-5.01421600	-0.66758200	-6.01916400
H	-5.50284100	-3.06599700	-5.58643500
H	-4.69896500	-4.14216800	-3.49506400
H	-3.40491500	-2.81755900	-1.83844800
H	-3.72056800	0.65234000	-4.35751200
C	1.09922600	-0.28483900	5.89062200
C	0.78146400	-1.62000200	6.15948900
C	0.11037600	-2.38852800	5.20295300
C	-0.24396400	-1.82373100	3.97881200
C	0.07236700	-0.48444100	3.70553400
C	0.74648100	0.28295300	4.66735900
C	-0.31490800	0.12254500	2.40320200
O	-0.03750900	1.34246200	2.14729200
O	-0.94074600	-0.56563200	1.52795200
H	1.61989300	0.31174100	6.63407700
H	1.05584600	-2.06102600	7.11378000
H	-0.13654100	-3.42531600	5.41225000
H	-0.76610400	-2.41241800	3.23180700

H	0.98779600	1.31856900	4.45182000
C	-0.31054100	7.46971400	-2.34041000
C	0.42317300	8.20205500	-1.40165500
C	0.83118800	7.60185100	-0.20618600
C	0.50758700	6.27066600	0.05131500
C	-0.22844400	5.53258600	-0.88783000
C	-0.63678800	6.13867100	-2.08548000
C	-0.56826500	4.10909200	-0.61813500
O	-1.24957500	3.43223000	-1.45827400
O	-0.17402200	3.54141400	0.45668900
H	-0.62654300	7.93605700	-3.26906100
H	0.67714600	9.23931600	-1.60165400
H	1.40098700	8.17089200	0.52268200
H	0.82155400	5.79732300	0.97572100
H	-1.20453500	5.56350200	-2.80941300