CITRATE COMPLEXES OF URANYL IN SOLUTIONS WITH HIGH CITRATE CONCENTRATIONS

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The composition and stability of uranyl citrate complexes in aqueous solutions of the ionic medium of 1M-$(H,Na,(UO_2)_{0\cdot5})A_3$ (where H_3A represents citric acid) were studied based on the potentiometric and spectrophotometric data. The best fit to the experimental data was obtained with the set of complexes UO_2A^-, $(UO_2A)_2^{2-}$, HUO_2A, $(HUO_2A)_2$, and $H_2UO_2A^+$, the former three complexes being significant in the whole concentration region.

The description of the extraction of some metal ions with amines from citrate solutions requires the recognition of the complex equilibria in the aqueous phases of the corresponding extraction systems. Since mineral acids salts suppress the extraction of citrates, the constancy of the activity coefficients of the aqueous phase components was ensured by using a constant ionic medium of 1M-$(H,Na,Me_{1/n}^{n+})_3A$, where H_3A denotes citric acid. In our previous works the dissociation constants of citric acid[1] and the stability constants of Fe(III) citrate complexes[2] were also determined in this medium.

The formation of uranyl citrate complexes has been studied by several authors[3-10]; in these works a constant ionic medium either was not maintained altogether[7,8] or was adjusted with mineral acids alkali salts[3-6], while Ohyoshi[9] maintained a constant (0·1M) concentration of sodium dihydrogencitrate and the H_2A^- ion.

A critical review of the published works has been presented by Markovits and coworkers[3]. The principal complex formed in citrate solutions of uranyl ions possesses the ratio $UO_2 : A = 1$. In earlier papers[7,10], this complex has been reported to be to a high degree dimerized or trimerized[10]. Newmann and coworkers[3,5] and Rajan and Martell[4] have considered the occurrence of both UO_2A^- and $(UO_2A)_2^{2-}$; the papers differ only in the dimerization constant reported. The course of the potentiometric titration curves for pH > 7 has been interpreted by Rajan and Martell[4] in terms of the polymeric hydroxo complexes of the core-links type. Feldman and coworkers[7,8] proved that at pH 4·6 no complexes with a higher proportion of the citrate ions are formed even if H_3A is present in a 1000-fold excess, whereas at pH 8 there exist also complexes with the $UO_2 : A$ ratio 1·5, probably in the dimer form. At lower pH (2·2—2·9), protonized complexes $UO_2H_2A^+$, UO_2HA, and UO_2A^- were found by Ohyoshi[9]. From the data cited, however, neither the composition of the complexes nor their stability in concentrated citrate solutions can be derived.

In this work, the uranyl complex formation was therefore studied in 1M-$(H, Na, (UO_2)_{0\cdot5})_3A$ at the uranyl concentrations $10^{-3}-10^{-1}$ mol/l. Under these conditions, the applicability of the potentiometric data is limited to the highest uranium concentrations because of the high buffer capacity of citrates. We had therefore to resort to spectrophotometric measurements, although they are less suitable for the study of more complex equilibria with possible oligomer formation[11], with regard to the high number of unknown constants (stability constants and molar absorptivities).

EXPERIMENTAL

Reagents

Citric acid, sodium citrate, uranium trioxide, and perchloric acid were reagent grade purity (Lachema). The stock solutions of citric acid and of sodium citrate were prepared and analyzed as in our previous works[1,2]. The uranyl citrate stock solution containing 0·5 mol/l UO_2^{2+} and 0·667 mol free citric acid was prepared by dissolving the weighed quantities of uranium trioxide and citric acid in redistilled boiled water and diluting to the volume. The uranium content in the stock solutions was determined spectrophotometrically according to Crouthamel and Johnson[12]. The solutions to be measured were prepared by mixing the corresponding volumes of the stock solutions. All uranium-containing samples were stored in darkness to prevent reduction resulting from photodecomposition.

Methods

The hydrogen ion concentration was measured by means of a combined glass-silver chloride electrode Metrohm EA-120U at 25 ± 0·05°C using a compensator Metrohm E 388 (ref.[2]). The pH values measured were corrected for the deviations caused by the liquid junction potential of the electrode. The latter was assumed to depend on the pH value solely in the system in question, and so it was determined for a system involving only H^+ and Na^+ cations from the pH value measured with the combined electrode in the solution of 1M-$(H,Na)_3A$ and that calculated by employing the citric acid protonation constants[1] in that medium ($\beta_1^H = 1{\cdot}8 \,.\, 10^5$, $\beta_2^H = 2{\cdot}5 \,.\, 10^9$, and $\beta_3^H = 1{\cdot}45 \,.\, 10^{12}$). The values of the corrections for the liquid junction potential thus obtained were applied for the same pH also to the uranyl-containing system.

The spectrophotometric measurements were carried out on a spectrophotometer Spekord UV-VIS (Zeiss, Jena) placed in a thermostatted room at 25 ± 1°C. Quartz cells 0·1–5 cm thick were used. As the blank served uranium-free 1M-$(H,Na)_3A$ solution of the same sodium citrate concentration as the solution measured.

RESULTS

Five series of solutions were prepared, having analytical concentration of uranium (c_U) 0·001, 0·004, 0·01, 0·04, and 0·1 mol/l, total concentration of the citrate ions 1 mol/l, and different concentrations of hydrogen ions. The pH values of the solutions lay in the range of 1·4–4·5; the lower limit was determined by the pH value of a 1M-H_3A solution (pH 1·39), the upper limit by the hydrolysis of the UO_2^{2+} ions and polymerization of the complexes formed, which, as indicated by the potentiometric data, is apparent in this system at pH > 4. For this reason, only the data obtained at pH 1·4–4·0 were taken into account during the calculations.

The absorption spectra of these solutions were measured and the absorbances

TABLE I

Dependence of the Absorbance per Unit Uranyl Concentration (ε_U) and pH on the Analytical Concentration of Hydrogen Ions (c_H) in Solutions of 1M-(H, Na, $(UO_2)_{0\cdot5})_3$ A

c_H mol/l	pH	ε_U (cm^{-1} mol^{-1}) for the wavenumbers, cm^{-1}					
		22 500	22 960	23 360	23 600	26 000	27 000
				0·1M-UO_2			
2·800	1·50	14·83	19·99	19·25	20·88	6·05	8·23
2·788	1·53	15·48	20·93	19·99	21·33	6·10	8·68
2·776	1·56	16·22	21·83	20·63	22·12	6·55	9·52
2·752	1·60	17·51	23·46	21·83	23·16	6·75	10·32
2·728	1·67	19·05	25·45	23·16	24·45	7·34	11·86
2·680	1·80	21·48	28·52	25·35	26·39	7·84	13·89
2·560	2·13	25·45	33·33	28·52	29·27	8·58	17·46
2·440	2·39	27·38	35·42	30·16	30·61	9·23	19·74
2·320	2·63	28·62	36·71	31·20	31·40	9·67	21·28
2·080	3·00	29·86	37·85	32·56	32·24	10·29	23·21
1·840	3·37	30·65	38·39	33·43	32·59	10·42	24·85
1·600	3·74	31·15	38·69	34·03	33·13	10·79	26·59
				0·04M-UO_2			
2·920	1·47	11·46	15·82	16·42	17·96	4·81	5·36
2·908	1·51	12·25	16·82	17·01	18·60	5·01	6·00
2·896	1·56	12·95	17·86	17·86	19·39	5·11	6·35
2·872	1·65	14·68	20·04	19·39	20·78	5·56	7·89
2·848	1·74	15·92	21·78	20·44	21·78	5·75	8·93
2·800	1·90	18·55	25·20	22·77	23·91	6·60	11·41
2·680	2·21	22·97	30·11	26·34	26·98	7·79	15·38
2·560	2·46	24·95	32·49	28·27	28·57	8·43	17·41
2·440	2·68	26·09	33·63	29·12	29·22	8·78	19·10
2·200	3·04	27·68	35·37	30·75	30·46	9·13	21·13
1·960	3·38	28·42	35·76	31·30	30·70	9·42	22·72
1·720	3·74	29·51	36·61	32·34	31·65	9·87	24·45
				0·01M-UO_2			
2·980	1·42	9·95	13·89	14·95	16·83	4·37	4·50
2·968	1·48	10·48	14·68	15·51	17·23	4·37	4·76
2·956	1·54	10·98	15·34	15·97	17·76	4·53	5·16
2·932	1·65	11·94	16·44	16·96	18·52	4·63	5·85
2·908	1·76	13·13	17·76	17·92	19·38	4·86	6·66
2·860	1·94	15·21	20·34	19·94	21·03	5·32	8·39
2·740	2·28	19·05	24·83	23·15	23·78	6·51	11·94
2·620	2·50	21·16	27·22	24·80	25·26	6·94	13·98
2·500	2·71	22·72	28·87	26·06	26·36	7·51	15·70
2·260	3·06	24·37	30·56	26·62	27·18	8·00	18·04
2·020	3·40	25·86	31·88	28·51	28·11	8·37	20·13
1·780	3·73	26·65	32·87	29·17	28·57	8·83	21·49

TABLE I
(*Continued*)

c_H mol/l	pH	ε_U (in cm^{-1} mol^{-1}) for the wavenumbers, cm^{-1}					
		22 500	22 960	23 360	23 600	26 000	27 000
				0·004M-UO_2			
2·992	1·41	9·57	13·34	14·58	16·42	4·71	4·27
2·980	1·47	10·22	14·09	15·33	17·21	4·76	4·71
2·968	1·53	10·52	14·38	15·63	17·41	5·06	4·86
2·944	1·64	11·06	15·18	16·17	17·86	5·26	5·06
2·872	1·93	13·34	18·01	18·30	19·74	5·31	6·50
2·752	2·26	16·02	21·48	20·78	22·17	5·65	8·83
2·632	2·49	17·91	23·86	22·62	23·46	6·15	10·81
2·512	2·70	19·54	25·69	23·91	24·60	6·60	12·55
2·272	3·03	21·58	28·17	25·74	26·09	6·89	14·48
2·032	3·37	22·82	29·51	26·69	26·69	6·89	15·82
1·792	3·72	24·45	30·80	28·22	28·03	8·13	18·20
				0·001M-UO_2			
2·998	1·40	8·61	12·28	13·57	15·38	—	—
2·986	1·46	9·40	13·29	14·78	16·53	—	—
2·974	1·52	9·31	13·13	14·56	16·53	—	—
2·950	1·65	9·88	14·19	15·28	17·12	—	—
2·926	1·75	10·24	14·46	15·56	17·40	—	—
2·878	1·94	11·45	16·17	17·22	19·01	—	—
2·758	2·26	12·70	17·24	18·06	19·44	—	—
2·638	2·50	13·77	19·37	19·37	20·54	—	—
2·518	2·69	14·23	19·82	19·64	20·83	—	—
2·278	3·04	16·65	22·14	21·43	22·02	—	—
2·038	3·39	17·92	23·41	22·22	23·02	—	—
1·798	3·72	18·57	24·21	22·90	23·21	—	—

(A) were read at the wavenumbers ($\tilde{\nu}$) 22500, 22960, 23360, 23600, 26000, and 27000 cm^{-1}. The data obtained are given in Table I, the pH values reported being corrected for the liquid junction potential. For $\tilde{\nu}$ = 22960 cm^{-1} the data are also shown in Fig. 1 as the plot of the absorbance per unit uranyl concentration (ε_U) *versus* the pH of the solution.

Determination of the Uranyl Molar Absorptivities in the Medium of 1M *Citrates*

The molar absorptivities of the UO_2^{2+} ions, $\varepsilon_{UO_2^{2+}}$, which are requisite for the subsequent calculations, cannot be determined in the system of 1M-(H, Na, $(UO_2)_{0.5})_3A$, because – as is apparent from the dependence of ε_U on the pH (Fig. 1) – an appreciable fraction of the uranyl ions is present in the form of complexes even for the highest acidity of this system, *i.e.* in pure H_3A solutions. The $\varepsilon_{UO_2^{2+}}$ values were therefore determined from the absorbances of solutions containing 1 mol/l H_3A, 0·01 or 0·1 mol/l UO_2^{2+}, and 0–2 mol/l $HClO_4$ (Table II, Fig. 2).

As is apparent from Fig. 2, in the range of 1-2M-$HClO_4$ the molar absorbance is nearly independent of the concentration of uranium as well as of perchloric acid. In this range, all the uranium can be thus assumed to be converted to the free UO_2^{2+} ion form, so that the $\varepsilon_{UO_2^{2+}}$ value can be calculated from the relation $\varepsilon_{UO_2^{2+}} = (A/c_U)_{2M-HClO_4}$. The $\varepsilon_{UO_2^{2+}}$ values found are given in Table III.

In fact, owing to the changes in the ionic strength the $\varepsilon_{UO_2^{2+}}$ value in 2M-$HClO_4$ may be somewhat different from that in 1M-$(H, Na)_3A$; however, this change does not affect appreciably the resulting values of the equilibrium constants or molar absorptivities of the citrate complexes, as $\varepsilon_{UO_2^{2+}}$ is at least five times less than the molar absorptivities of the citrate complexes.

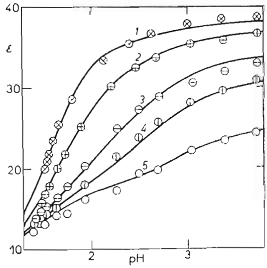

FIG. 1

Dependence of the Absorbance at 22960 cm^{-1} of the Solution per Unit Uranyl Concentration (ε_U) on the pH of the 1M-(H,Na,$(UO_2)_{0.5})_3$ Solution

c_U (mol/l): *1* 0·1, *2* 0·04, *3* 0·01, *4* 0·004, *5* 0·001. Solid lines: theoretical curves calculated for the set of complexes (0,1,1), (0,2,2), (1,1,1), (2,2,2), (2,1,1) – stability constants as given in Table III.

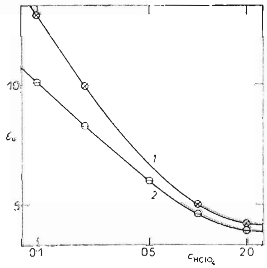

FIG. 2

Dependence of the Absorbance at 22960 cm^{-1} of the Solution per Unit Uranyl Concentration (ε_U) on the Concentration of Perchloric Acid

c_U (mol/l): *1* 0·1, *2* 0·01.

TABLE II

Dependence of the Absorbance per Unit Uranyl Concentration (ε_U) on the Concentration of Perchloric Acid (c_{HClO_4}) in Solutions of 1M-(H, $(UO_2)_{0\cdot5})_3A$ + $HClO_4$

c_{HClO_4} mol/l	ε_U for the wavenumbers, cm^{-1}					
	22 500	22 960	23 360	23 600	26 000	27 000
			0·105M-UO_2			
0·0	13·89	18·44	18·09	19·31	5·85	7·90
0·1	9·35	12·90	14·04	15·38	4·89	4·70
0·2	7·08	9·96	11·52	12·60	4·39	3·56
1·0	3·51	5·03	6·92	7·31	3·32	2·70
2·0	2·92	4·23	6·30	6·45	3·08	2·60
			0·0105M-UO_2			
0·0	9·75	13·82	15·32	16·94	5·31	4·73
0·05	8·51	11·63	13·47	15·01	5·14	4·19
0·10	7·33	10·10	12·00	13·30	4·86	3·83
0·20	5·88	8·29	10·26	11·24	4·42	3·49
0·50	4·32	5·98	8·28	8·77	4·13	3·40
1·00	3·20	4·63	7·00	7·30	3·55	2·95
2·00	2·72	3·93	6·30	6·46	3·27	2·84

TABLE III

Molar Absorptivities of the UO_2^{2+} Ion and Uranyl Citrate Complexes in 1M-(H, Na, $(UO_2)_{0\cdot5})_3A$ at Different Wavenumbers

The precision is given as ±s(ε), where s(ε) is the standard deviation of the absorptivity calculated from all data of Table I.

Species	Molar absorptivity (in 1 cm^{-1} mol^{-1}) for the wavenumber, cm^{-1}					
	22 500	22 960	23 360	23 600	26 000	27 000
$UO_2H_2A^+$	12·2 ± 0·3	16·9 ± 0·3	18·2 ± 0·3	21·3 ± 0·3	4·9 ± 0·2	3·9 ± 0·3
UO_2HA	12·9 ± 0·4	18·2 ± 0·5	18·2 ± 0·4	19·5 ± 0·4	5·3 ± 0·4	7·8 ± 0·7
$(UO_2HA)_2$	90·4 ± 2	118 ± 2	89·6 ± 2	88·5 ± 2	27·6 ± 1·4	59·7 ± 2
UO_2A^-	9·8 ± 0·7	13·6 ± 0·7	15·8 ± 0·6	16·5 ± 0·5	1·2 ± 0·8	2·4 ± 1·8
$(UO_2A)_2^{2-}$	64·9 ± 0·7	80·7 ± 0·7	68·8 ± 0·6	67·5 ± 0·5	22·1 ± 0·5	52·6 ± 1
UO_2^{2+}	2·84	4·16	6·40	6·52	3·20	2·64

Determination of the Charge of the Uranyl Citrate Complexes from the Potentiometric Data

In the pH region of 3·5 – 4, the absorbances of the 1M-(H, Na, $(UO_2)_{0.5})_3A$ solutions containing uranyl in concentrations 0·01 – 0·1 mol/l are approximately constant, which implies that only one uranyl complex species occurs in this concentration region.

Since, as found by Neuman and coworkers polarographically[8], uranyl does not form complexes containing more than one citrate ion per one uranyl ion even if the citrates are present in a 1 000-fold excess, $(H_xUO_2A)_n$ type complexes can be assumed to occur in this region. If the complexes are thus of the composition $UO_2 : A = 1 : 1$, the number of the hydrogen ions bonded to one UO_2^{2+} ion, x, and thereby also the charge of the complex can be determined from the potentiometric data according to the relation derived[2] based on the concentration and charge balance:

$$x = 1 - (h + [Na^+])/c_U + (c_A - c_U)(\beta_2 h^2 + 2\beta_1 h + 3)/((1 + \beta_1 h + \beta_2 h^2 + \beta_3 h^3)\, c_U)\,, \qquad (1)$$

where $h (= 10^{-pH})$ is the concentration of free protons, $[Na^+]$ is the concentration of the sodium ions, which virtually equals the analytical concentration of sodium, c_A and c_U are the analytical concentrations of the citrate and uranyl ions, respectively, and β_n's are the overall stability constants of citric acid in the 1M-$(H, Na)_3A$ system.

From Eq. (*1*), $x = -0·1 \pm 0·1$ was obtained in the region pH = 3·3 – 4 and $c_U = 0·04 - 0·1$ mol/l, hence most of the uranyl ions occur in this region in the form of the $(UO_2A)_n^{n-}$ complexes.

Determination of the Dimerization Constant of the $(UO_2A)_n^{n-}$ *Complex by Means of the Linear Transformation Method*

The curves $\varepsilon_U = f(pH)$, Fig. 1, are shifted upwards with increasing c_U, which can be explained in terms of the polymerization of the corresponding complex, the molar absorptivity of the polymerized complex being higher than that of the monomer.

Provided that the highest polymerization degree is 2, it is possible to determine for the dimerization reaction

$$2\,UO_2A^- \rightleftharpoons (UO_2A)_2^{2-} \qquad (A)$$

the equilibrium constant K_d:

$$K_d = [(UO_2A)_2^{2-}]/[UO_2A^-]^2 \qquad (2)$$

by using the linear transformation method[11]. For this purpose, the dependences

$$\varepsilon_U = \varepsilon_1 - K_d c_U(2\varepsilon_U - \varepsilon_2)^2/(2\varepsilon_1 - \varepsilon_2) \quad (3)$$

$$\varepsilon_U = \varepsilon_2/2 + ((2\varepsilon_1 - \varepsilon_2)(\varepsilon_1 - \varepsilon_U)/2K_d c_U(2\varepsilon_U - \varepsilon_2)) \quad (4)$$

were employed.

If the assumption of the occurrence of two complex species only, *i.e.* the monomer and the dimer (absorptivities ε_1 and ε_2, respectively), is correct, the dependences

$$\varepsilon_U = f(c_U(2\varepsilon_U - \varepsilon_2)^2/(\varepsilon_2 - 2\varepsilon_1)) \quad (5)$$

form a straight line of the slope K_d and intercept ε_1. Analogously the dependence

$$\varepsilon_U = f((\varepsilon_1 - \varepsilon_U)(2\varepsilon_1 - \varepsilon_2)/2(2\varepsilon_U - \varepsilon_2)\, c_U) \quad (6)$$

represents a straight line whose slope is $-1/K_d$ and intercept $\varepsilon_2/2$.

The ε_2 values were obtained by iterative variation so that the dependences (*5*) be linear. The ε_1 or ε_2 values obtained from the dependences (*5*) and (*6*) were then usually the same; in case that they differed, a single iterative step was usually sufficient to obtain correct values.

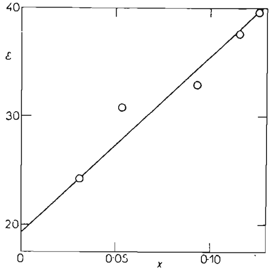

FIG. 3

Calculation of the Molar Absorptivities ε_1 and ε_2 and of the Dimerization Constant K_d for the Dimerization of the Complex UO_2A^- by Means of the Linear Transformation Method According to Eq. (*5*) for the Wavenumber $\tilde{\nu} = 22960\ cm^{-1}$
$x = c_U(2\varepsilon_U - \varepsilon_2)^2/(\varepsilon_2 - 2\varepsilon_1)$.

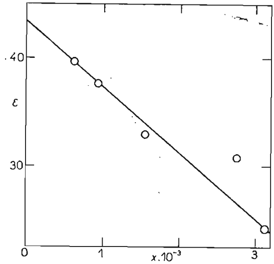

FIG. 4

Calculation of the Molar Absorptivities ε_1 and ε_2 and of the Dimerization Constant K_d for the Dimerization of the Complex UO_2A^- According to Eq. (*6*) for the Wavenumber $\tilde{\nu} = 22960\ cm^{-1}$
$x = (\varepsilon_2 - 2\varepsilon_1)(\varepsilon_1 - \varepsilon_U)/2c_U(2\varepsilon_U - \varepsilon_2)$.

This calculation for the data of Fig. 1 is shown in Figs 3 and 4. The dependences (*5*) and (*6*) are seen to be really nearly linear, so that the concept of the formation of the $(UO_2A)_n^{n-}$ complexes with $n = 1$ and 2 can be adopted as the principal equilibrium in the system studied. The average value of the dimerization constant determined in the pH region of 3·6 – 3·7 is $\log K_d = 2{\cdot}35^{+0.38}_{-0.22}$. The values of ε_1 and ε_2 for $\tilde{\nu} = 22500 - 23600 \text{ cm}^{-1}$ are given in Table III.

Refinement of the Interpretation by Computer Data Processing

In the preceding paragraphs, UO_2A^- and $(UO_2A)_2^{2-}$ were determined graphically to be the predominating complexes. In order to verify this interpretation, *i.e.* to seek if the above set is sufficient for the treatment of all the experimental data and their possible extention, numerical calculations were undertaken using the program LETAGROP-SPEFO (ref.[13]), as has been done previously[2] for Fe(III) citrate complexes. To save computation time, the variation of the citrate concentration resulting from the bonding to the metal was disregarded in the overall mass balance.

The adequacy of the various sets of complexes was assessed *via* the sum of the squares of the deviations between the observed and calculated absorbance values (U).

In the further text, the simplified symbol (p, q, r) will stand for the complex $H_p(UO_2)_qA_r$.

The simplest model of two complexes, UO_2A and $(UO_2A)_2^{2-}$ – hence (0, 1, 1) and (0, 2, 2) – was tested first; the agreement with the experimental curve was found insufficient. The set of complexes was then augmented with protonized species, as suggested also by Ohyoshi[9] on the base of cation exchanger studies. Protonized citrate complexes are formed also with many other metals[14,15]. The best fit was achieved with the combination of complexes (0, 1, 1), (0, 2, 2), (1, 1, 1), (2, 2, 2), and (2, 1, 1) ($U = 0{\cdot}311$). A close U value was obtained also with the combination (0, 1, 1), (0, 2, 2), (1, 1, 1), and (2, 2, 2); however, a physically unlikely molar absorptivity value ($>10^6$) emerged for the last complex. The combination of the complexes (0, 1, 1), (0, 2 2), and (1, 1, 1) gave $U = 0{\cdot}396$, and the combination (0, 1, 1), (0, 2, 2), (2, 2, 2), and (2, 1, 1) gave $U = 0{\cdot}569$. More elaborate models were not tested.

The conclusions concerning the composition of the complexes obtained from the spectrophotometric data were verified by processing the acidity data of some solutions (Table I, series with $c_{UO_2} = 0{\cdot}1$ and 0·04 mol/l and six points from the acidic region of the series with $c_{UO_2} = 0{\cdot}01$ mol/l) by means of the program[16] LETAGROP-ETITR;

Minimized was the difference between the calculated and observed total analytical concentrations of acidic hydrogen. The input set (0, 1, 1), (0, 2, 2), (1, 1, 1), (2, 2, 2), and (2, 1, 1) reduced during the computation to (0, 1, 1), (0, 2, 2), and (1, 1, 1), as the minimum of the U function was reached for zero values of the stability constants of the complexes (2, 2, 2) and (2, 1, 1). The obtained stability constants for

TABLE IV

Comparison of the Adequacy of the Various Models of Complex Equilibria in 1M-(H, Na, $(UO_2)_{0\cdot5})_3$A Suggested in This Work and Some Published Data for the Range pH < 4

Set of complexes	log β of the complexes[a]	U	Method[b]	Medium[c]	c_U mol/l	pH	Ref[d]
(0, 1, 1), (0, 2, 2), (1, 1, 1), (2, 2, 2), (2, 1, 1)	6·20 max 6·47; 15·25 max 15·69; 9·07 max 9·34; 19·40 max 19·63; 10·90 ± 0·25	0·313	sp		0·001—0·1	1·4—4·0	
(0, 1, 1), (0, 2, 2), (1, 1, 1), (2, 2, 2)	leads to unlikely high ε value of the complex (2,2,2)	0·344	sp		0·001—0·1	1·4—4·0	
(0, 1, 1), (0, 2, 2), (1, 1, 1)	7·17 ± 0·16; 17·00 ± 0·14 9·81 ± 0·07	0·396	sp		0·001—0·1	1·4—4·0	
(0, 1, 1), (0, 2, 2), (1, 1, 1)	6·92 max 7·80; 16·86 max 17·20; 9·68 ± 0·26	687[e]	pot		0·01—0·1	1·4—3·7	
(0, 1, 1), (0, 2, 2), (2, 2, 2), (2, 1, 1)	6·08 max 6·27; 14·80 max 15·10; 20·34 max 20·61; 11·43 ± 0·21	0·569	sp		0·001—0·1	1·4—4·0	
(0, 1, 1), (0, 2, 2)	6·28; 17·57		pot	1M-KNO_3	$3 . 10^{-5}—10^{-3}$	2·8—4·2	3
(0, 1, 1), (0, 2, 2)	6·9 ± 0·1; 17·7 ± 0·04		pot	1M-KNO_3	$8 . 10^{-4}—1\cdot6 . 10^{-2}$	2—4	4
(0, 1, 1), (1, 1, 1), (2, 1, 1)	7·28; 9·90; 12·85		cex	0·1M-NaH_2A	$10^{-6}—10^{-5}$	2·2—2·9	9

[a] The precision of the constant is given as ±3s (β), where s(β) is the standard deviation of the constant β. If s(β) > 0·2β, then only the upper limit, *i.e.* β + 3s(β), is given, which is expressed in the table as β max (β + 3s(β)); [b] sp — spectrophotometry, pot — potentiometry, cex — by means of cation exchangers; [c] 1M-(H, Na, $(UO_2)_{0.5})_3$A unless stated otherwise; [d] this work unless stated otherwise; [e] the calculation has been performed for the potentiometric data, thus the U value cannot be compared with that obtained from the spectrophotometric data; the U value expressed from the same constants for the spectrophotometric data is U = 0·477.

the sef (0, 1, 1), (0, 2, 2), and (1, 1, 1) approach those calculated for the same set from the spectrophotometric data.

The results are listed along with some published data in Table IV.

DISCUSSION

From a comparison of the models given in Table IV, the complexes UO_2A^-, $(UO_2A)_2^{2-}$, and HUO_2A emerge as the most significant; their constants are also best defined, as is apparent from the set where only these three complex species were considered. Owing to the fact that the data fall into regions of higher acidities as well as of higher c_U concentrations, the higher protonized (2, 1, 1) complex found also by Ohyoshi[9] and the polymerized protonized complex of the (2, 2, 2) composition play an important part too.

A degree of inaccuracy of some constants is due to the way of processing of the spectrophotometric data. The unknowns β_{pqr} and ε_{pqr} appear in product in the expression for the U function, thus an error in β, for instance, can be partly compensated by the change of the ε values. Also, complexes whose linear molar absorptivities possess nearly equal values are poorly discriminated. This applies particularly to the complex (2, 1, 1), inasmuch as the $\varepsilon_{2,1,1}$ value approaches that of $\varepsilon_{1,1,1}$ and moreover,

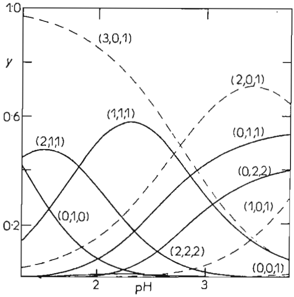

FIG. 5

Fractions of the Individual Complexes $H_p(UO_2)_qA_r$ ((p, q, r)) out of the Total Uranyl Concentration (y) in Dependence on the pH of the System of 1M-(H,Na, $(UO_2)_{0.5})_3A$ for $c_U = 0{\cdot}001$ mol/l

----- fraction of the citric acid anions out of the total citric acid concentration.

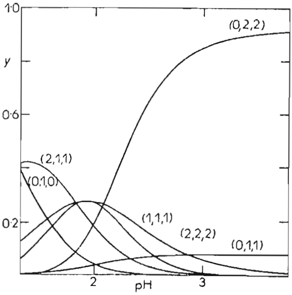

FIG. 6

Fractions of the Individual Complexes $H_p(UO_2)_qA_r$ ((p, q, r)) out of the Total Uranyl Concentration (y) in Dependence on the pH of the System of 1M-$(H,Na(UO_2)_{0.5})_3A$ for $c_U = 0{\cdot}1$ mol/l in the system in question it is not possible to measure at pH $< 1{\cdot}39$, where the proportion of the (2, 1, 1) complex would be greater. The potentiometric data in the series with $c_U = 0{\cdot}1$ and 0·04 mol/l are satisfied by a value of the $\beta_{2,1,1}$ constant at least one order of magnitude lower than as results from the spectrophotometric data. Although the error in the $\beta_{2,1,1}$ constant can be to a degree reflected in the other constants too, its effect is not too great, as is obvious from the values of the constants for the different models.

The fractions of the individual complexes with respect to the total uranyl concentration in dependence on the pH are given for the two limiting uranyl concentrations, $c_U = 0{\cdot}001$ and 0·1 mol/l (Figs 5 and 6, respectively). Fig. 5 presents in addition also the concentrations of the individual citric acid ion species calculated for a uranyl-free solution. The dependence of the concentration change on the pH is nearly parallel for the following groups of ions of citric acid and citrate complexes:

$$(3, 0, 1) - (1, 1, 1) + (2, 2, 2)$$
$$(2, 0, 1) - (0, 1, 1) + (0, 2, 2)$$

In both pairs, the monomeric uranyl citrate complex can be formally derived by replacing two protons in the pertinent citric acid ion by an uranyl ion: for instance, the H_2A^- ion converts to the UO_2A^- complex, which dimerizes to give $(UO_2A)_2^{2-}$. A region of the hydrogen ion concentrations is thus associated with a certain valency of the complex, irrespective of whether the ligand is proton or metal ion bonded. With this is also related the fact that the equilibrium constants of the ion exchange for protons according to the reactions

$$H_3A + UO_2^{2+} \rightleftharpoons HUO_2A + 2\,H^+ \qquad (B)$$
$$H_2A^- + UO_2^{2+} \rightleftharpoons UO_2A^- + 2\,H^+ \qquad (C)$$

are almost identical, *viz.* $10^{-3.0}$ for the reaction (*B*) and $10^{-3.2}$ for the reaction (*C*).

The dimerization of the unprotonized complex (0, 1, 1) is more pronounced than that of the complex (1, 1, 1); the respective dimerization constants are $\log K_{d(0,1,1)} = 2{\cdot}85$ and $\log K_{d(1,1,1)} = 1{\cdot}26$. The reason why the dimerization of the former complex proceeds more readily lies in the fact that prerequisite for the formation of polymeric structures[4] is the occurrence of a dissociated carbonyl group.

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