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Complex Formation between the Uranyl Ion and Citric Acid

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A method to facilitate the analysis of the complex formation by a polybasic acid has been applied to the study of uranyl citrate complexes. The amount of the uranyl ion in equilibrium with the complexing agent was determined by the cation-exchange method. In this experiment, the uranyl-ion concentration was kept within a 10^{-5}—10^{-6} M range in order to eliminate polymeric species. By using a series of solutions prepared so as to keep $[H_3Cit^-]$ nearly constant and to vary $[H_2Cit^{2-}]$ and $[HCit^{3-}]$ in the 2.2—2.9 pH range, it has been found that three kinds of complexes, $UO_2H_3Cit^+$, UO_2H_2Cit, and UO_2HCit^-, were present in the solution. Approximate values of their formation constants were obtained.

In an investigation[1] of the photochemical reduction of U(VI) to U(IV) observed in citrate solutions, knowledge of the nature of uranyl citrate complexes and of their formation constants was required for the interpretation of the reduction mechanism. On the basis of potentiometric measurements, Rajan and Martell[2] reported that, in the 2—4 pH range, the uranyl ion combined through the dissociation of the three hydrogens from the carboxyl groups of citric acid, and also that the dimerization of this complex occurred with an increase in the uranyl-ion concentration. In this pH range, more protonated species, H_3Cit^- and H_2Cit^{2-}, are present in large proportions, and they possibly form complexes with the uranyl ion.

Matsushima[3] has studied the citrate complexes of some divalent metals by an extension of Schubert's method to a lower pH region. He found the complex of the MH_2Cit type as well as that of the $MHCit^-$ type and determined the stability constants of both. In this method, however, it is necessary to perform similar experiments at several different pH's, each of which is kept constant for the analysis of the different types of complexes.

In the present work, we have studied the complex formation between uranyl and various protonated citrate ions in a region of low concentrations of the uranyl ion by using a method devised to facilitate the analysis of the complexes with a polybasic acid.[4] The method used is based on the general principles of dissociation equilibria established in the presence of a weak acid and its salt.

Analysis of Metal (M^{2+}) Complexes Formed with Various Protonated Species. In our earlier papers[4,5] we assumed that only two species, H_3Cit^- and H_2Cit^{2-}, are advantageous for the formation of complexes in a low-pH region. However, as has been shown by the potentiometric study,[2] the complex of the UO_2HCit^- type cannot be excluded even at pH 2. Therefore, we have derived equations assuming three types of complexes, $M(H_3Cit)_i^{2-i}$, $M(H_2Cit)_j^{2-2j}$, and $M(HCit)_k^{2-3k}$, equilibrated in solution. When we use the cation-exchange method and can assume that the adsorption of the MH_3Cit^+ complex is negligible compared with that of the M^{2+} ion at a low ionic strength of 0.1 or 0.2,[6] the following equation can be derived:

$$\frac{K_d^\circ}{K_d} = 1 + \sum\beta_i[H_3Cit^-]^i + \sum\beta_j'[H_2Cit^{2-}]^j + \sum\beta_k''[HCit^{3-}]^k \qquad (1)$$

where K_d° and K_d denote the distribution coefficients of uranyl species in the absence and in the presence of the complexing agent respectively, and where β_i, β_j', and β_k'' express the formation constants of the $M(H_3Cit)_i^{2-i}$, $M(H_2Cit)_j^{2-2j}$, and $M(HCit)_k^{2-3k}$ complexes respectively. When experiments were carried out by using a series of solutions in which the amount of the H_3Cit^- species remains nearly constant, while those of the H_2Cit^{2-} and $HCit^{3-}$ species vary, Eq. (1) can be given as a function of $[H_2Cit^{2-}]$ or $[HCit^{3-}]$:

$$\frac{K_d^\circ}{K_d} - 1 = \text{const.} + (\beta_1' + \beta_1''k_3/[H^+])[H_2Cit^{2-}] + (\beta_2' + \beta_2''k_3^2/[H^+]^2)[H_2Cit^{2-}]^2 + \cdots \qquad (2)$$

or;

$$\frac{K_d^\circ}{K_d} - 1 = \text{const.} + (\beta_1'' + \beta_1'[H^+]/k_3)[HCit^{3-}] + (\beta_2'' + \beta_2'[H^+]^2/k_3^2)[HCit^{3-}]^2 + \cdots \qquad (3)$$

where $k_3 = [H^+][HCit^{3-}]/[H_2Cit^{2-}]$. When we assume that all the complexes have a 1:1 molar ratio, Eqs. (2) and (3) are simplified as follows:

$$\frac{K_d^\circ}{K_d} - 1 = \text{const.} + (\beta_1' + \beta_1''k_3/[H^+])[H_2Cit^{2-}] \qquad (4)$$

$$\frac{K_d^\circ}{K_d} - 1 = \text{const.} + (\beta_1'' + \beta_1'[H^+]/k_3)[HCit^{3-}] \qquad (5)$$

From Eqs. (4) and (5), it can be seen that when we plot $K_d^\circ/K_d - 1$ *vs.* $[H_2Cit^{2-}]$ (A) or *vs.* $[HCit^{3-}]$ (B), two different types of curves should be obtained. The slope of the (A) plot increases with a decrease in $[H^+]$, while that of the (B) plot decreases with a decrease in $[H^+]$. The intercepts of both plots should be the same value. From this value and the $[H_3Cit^-]$ used, β_1 can be evaluated. Approximate values of β_1' and β_1'' can also be estimated from the slope of (A) at $[H_2Cit^{2-}] = 0$ and from the slope of (B) at the relatively high value of $[HCit^{3-}]$, sufficient to show a straight line, respectively. In cases where successive complex formation takes place, we can obtain a similar curve, (A) or (B), by plotting the $(K_d^\circ/K_d - 1 - \text{const.})/[H_2Cit^{2-}]$ term *vs.* $[H_2Cit^{2-}]$ or the $(K_d^\circ/K_d - 1 - \text{const.})/$

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$[HCit^{3-}]$ term *vs.* $[HCit^{2-}]$; β_2' and β_2'' can also be estimated in a similar manner. A separate experiment will be necessary to obtain β_1 and β_2. The solutions used for this experiment can be prepare by varying the total citrate concentration at a constant pH, since we have already established the complexing ability of both ligands, H_2Cit^{2-} and $HCit^{3-}$.

Experimental

Materials. The stock solution of UO_2^{2+} was prepared by dissolving $UO_2(NO_3)_2 \cdot 6H_2O$ in 0.005 M HCl to give the concentration of 2.0×10^{-4} M, which was determined by EDTA titration. Citric acid (H_4Cit) in varying amounts was added to 0.2 M NaH_3Cit. A series of such solutions was diluted twice with distilled water and the uranyl stock solution. In these solutions, H_2Cit^{2-} and $HCit^{3-}$ decrease with an increase in the H_4Cit, while H_3Cit^- is maintained nearly constant (0.1 M). The ionic strength, governed by the amount of the salt, NaH_3Cit, was also maintained at 0.1. The compositions of the solutions used are given in Table 1. For the calculation of the respective ion concentrations, the dissociation constants of citric acid reported by Okac and Kolarik,[7] which were measured at $\mu=0.1$ (0.1 M KCl) and 8—20 °C, were used. The pH values calculated using this k_1 value and the amounts of acid H_4Cit and salt NaH_3Cit dissolved were in fair agreement with the measured pH values. Various concentrations of citrate at a constant pH of 3.91 were prepared by dissolving a mixture of H_4Cit and Na_3HCit (1.5: 1) in 0.1 M $NaClO_4$ to produce concentrations of $HCit^{3-}$, 10^{-5}—10^{-6} M. All the chemicals used were of a G. R. grade. The pH measurements were made with a Beckman Model SS-2 pH meter. A cation exchanger, Dowex 50 W-X8 (100—200 mesh), in sodium form was used.

TABLE 1. THE COMPOSITION OF CITRATE SOLUTIONS PREPARED TO MAINTAIN $[H_3Cit^-]$ NEARLY CONSTANT (0.1M)

$[H_4Cit]$ (M)	$[H_3Cit^-]$ (M)	$[H_2Cit^{2-}]$ (10^{-3} M)	$[HCit^{3-}]$ (10^{-6} M)	pH
0.600	0.103	0.65	0.22	2.19
0.484	0.102	0.79	0.32	2.28
0.360	0.102	1.07	0.58	2.41
0.237	0.101	1.58	1.30	2.59
0.202	0.101	1.85	1.75	2.65
0.166	0.100	2.23	2.64	2.74
0.143	0.99	2.55	3.47	2.80
0.118	0.99	3.06	5.02	2.88

Procedure. The cation-exchange experiments were carried out in a manner similar to that described previously.[4] The amount of U(VI) was determined as the uranyl-Arsenazo-(III) complex by spectrophotometry using a Shimadzu UV-200 spectrophotometer. This complex was stable even at pH 1, and its characteristic color (absorbance at 665 nm) could be used to determine the U(VI) in the presence of citric acid. Since the slope of the calibration curve slightly varied with the pH value, it was necessary to measure the absorbance of aliquots of slutions before the addition of the cation exchanger and after equilibrium had been reached at a constant pH. All the experiments were carried out in the dark to avoid any photochemical reduction of the uranyl ion.[1] The distribution coefficient, K_d, was calculated as follows:

$$K_d = \frac{\text{mmol of U(VI) in the resin/mass of dry resin (g)}}{\text{mmol of U(VI) in the soln./vol. of soln. (ml)}}$$

Results and Discussion

The hydrolyses of the uranyl ion in the pH range studied (pH 2—4) were checked by measuring $K_d°$ in 0.1 M $NaClO_4$, while adjusting pH's from 2.07 to 4.35. To maintain the pH at 4.35, the acetate buffer in varying concentrations ($\sim 10^{-3}$ M) was used. $K_d°$ was obtained by plotting $1/K_d$ *vs.* [acetate] and by extrapolating $1/K_d$ to a zero concentration of acetate. $K_d°$ values so obtained were practically constant ($2.3 \pm 0.1 \times 10^3$), indicating that hydrolysis does not occur in this pH range.

To check whether polymeric species were being formed or not, the K_d values were determined as a function of [U(VI)] at constant citrate concentrations. The results showed that, at pH 3.91, K_d gradually decreased at concentrations above 1×10^{-5} M, though it remained practically constant at lower pH's (2.2—2.9), indicating that polymeric species tend to be formed as the pH increases. The uranyl concentrations used in this experiment were in the 4×10^{-6}—6×10^{-6} M range at pH 3.91 and in the 6×10^{-6}—1×10^{-5} M range at pH's 2.2—2.9. The constancy of K_d was also obtained with a variation in the ratio of the volume of the solution to the mass of resin from 50—200 ml/g.

Using a series of solutions in a region of low pH's (2.2—2.9) where $[H_3Cit^-]$ is kept approximately constant ($[H_3Cit^-] \simeq 0.1$), and where $[H_2Cit^{2-}]$ and $[HCit^{3-}]$ both vary, uranyl citrate complexes have been studied by the cation-exchange method.

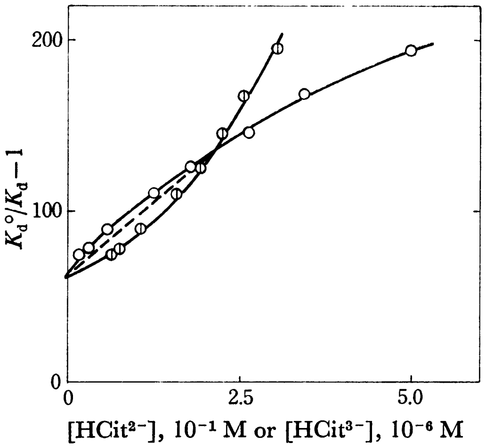

Fig. 1. Plots of $K_d°/K_d-1$ *vs.* $[H_2Cit^{2-}]$ and $[HCit^{3-}]$ at $[H_3Cit^-]=0.1$ M and various pH values.

As is shown in Fig. 1, where we tried to plot $K_d°/K_d-1$ as a function of $[H_2Cit^{2-}]$ (Plot A) or $[HCit^{3-}]$ (Plot B), the slope of Plot A increases with a decrease in $[H^+]$ while that of Plot B decreases with a decrease in $[H^+]$, and both plots have the same intercept. To examine the type of complex predominantly formed, a separate experiment was carried out using solutions in varying total citrate concentrations in the same range and at a constant pH of 2.88. From the fact that a linear relationship was obtained between $K_d°/K_d-1$

and $[\text{Citrate}]_{\text{total}}$, it can be concluded that 1 : 1 complexes are the only predominantly-formed species.[3] Hence, the former type of curve (Plot A) corresponds to Eq. (4), while the latter (Plot B) corresponds to Eq. (5). From this it is evident that the $UO_2H_3Cit^+$, UO_2H_2Cit, and UO_2HCit^- complexes are all present in this pH range (2.2—2.9). At pH 2.28, where a major part of the complexes are assumed to be $UO_2H_3Cit^+$ from the curves in Fig. 1, the extent of adsorption of this species on the cation exchanger was studied at different ionic strengths of 0.1 and 0.2.[6] The results showed that the adsorption of $UO_2H_3Cit^+$ on the cation exchanger was negligible compared with that of UO_2^{2+} at these low ionic strengths. The formation constant of $UO_2H_3Cit^+$, β, can readily be obtained from the intercept of the two curves in Fig. 1, which equals 0.1β. The approximate values of β' and β'', the formation constants of UO_2H_2Cit and UO_2HCit^-, can be obtained, respectively, from the slope of Plot (A) at $[H_2Cit^{2-}]=0$ and from that of Plot (B) at relatively large values of $[HCit^{3-}]$, where Plot (B) approaches a straight line. The values of β, β', and β'' thus obtained are listed in Table 2.

At higher pHs, where almost all the uranyl complexes can be assumed to be of the UO_2HCit^- type we can estimate β'' with considerable accuracy. Figure 2 shows a plot of $(K_d{}^\circ/K_d-1)$ *versus* $[HCit^{3-}]$ at a constant pH of 3.91. The value of β'' calculated from the slope is also listed in Table 2. From the fact that the two values of β'' obtained by the different methods are in fair agreement, the method used in this study can be said to be applicable to the analysis of complexes formed with various protonated ligands present in a solution. The reliability of the β' thus obtained can be checked by the slope of the broken line in Fig. 1. Judging from Eqs. (4) and (5), when we plot the relations (A and B) taking a scale of $[H_2Cit^{2-}]$ equal to $10^3[HCit^{3-}]$, the two curves, A and B, should cross at $[H^+]=10^3k_3$, where $[H_2Cit^{2-}]=10^3[HCit^{3-}]$, and the slope of the broken line can be said to correspond to $\beta'+10^{-3}\beta''$ or $\beta''+10^3\beta'$ on the scale of $[H_2Cit^{2-}]$ or of $[Cit^{3-}]$ respectively. From these values and the β'' value obtained at pH 3.91, a more accurate value of β' can be calculated; it is also presented in Table 2. The two values of β' in Table 2 are in fair agreement.

TABLE 2. FORMATION CONSTANTS OF UO_2–CITRATE COMPLEXES (μ=0.1, 25 °C)

	$UO_2H_3Cit^+$ logβ	UO_2H_2Cit logβ'	UO_2HCit^- logβ''
Present work	2.79	4.26[a]	7.28[a]
		4.23[b]	7.22[c]
Reference values	—	—	7.40[2]
	—	—	8.6[8]
	—	—	3.16[9]

a) The approximate values estimated from the slope of the curve A or B. b) The calculated value from the slope of the dotted line and β''. c) The value obtained at pH 3.91.

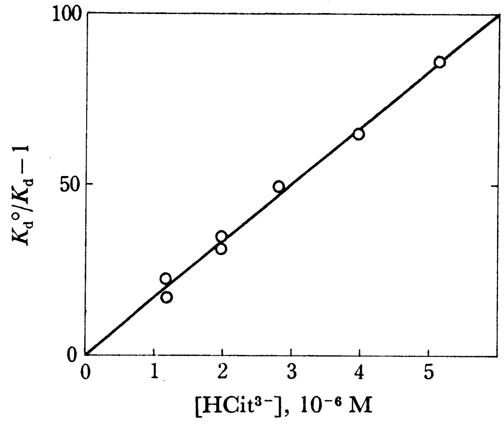

Fig. 2. A plot of $K_d{}^\circ/K_d-1$ *vs.* $[HCit^{3-}]$ at pH 3.91.

For the formation constant of UO_2HCit^-, various values[2,8,9] have been reported. As is shown in Table 2, the logarithmic value of the formation constant contained in this study is in fair agreement with that determined potentiometrically by Rajan and Martell.[2] There are no published data for the formation constants of $UO_2H_3Cit^+$ and UO_2H_2Cit because three different complexes, $UO_2H_3Cit^+$, UO_2H_2Cit, and UO_2HCit^-, coexisting at low pH's could not be analyzed.

In conclusion, by controlling the concentration of H_3Cit^- in the solution, various species of uranyl citrate could easily be analyzed, and each formation constant could also be determined. The fraction of the species varying with the pH could be evaluated by considering these constants. The predominant species at pH's lower than 2 was $UO_2H_3Cit^+$. There was a mixture of $UO_2H_3Cit^+$, UO_2H_2Cit, and UO_2HCit^- in the pH range of 2—3, and at pH's higher than 3 almost all of the species were UO_2HCit^-.

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