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Formation Constants for the Mixed-Metal Complexes between Indium(III) and Uranium(VI) with Malic, Citric, and Tartaric Acids[1]

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Formation constants have been determined for the mixed-metal complexes between indium(III) and uranium(VI) with malic, citric, and tartaric acids. In the cases of malic and tartaric acids the equilibrium can be written as $UO_2^{2+} + In^{3+} + 2H_3L = UO_2InL_2^- + 6H^+$. The logarithms of the equilibrium constants are −7.62 for the malate system and −7.14 for the tartrate. In the case of citric acid the equilibrium is $UO_2^{2+} + In^{3+} + 2H_4L = UO_2InL_2^{3-} + 8H^+$ where two of the protons come from the hydroxy groups. The logarithm of the constant is −11.58. Infrared measurements on trilaurylamine extracts of the mixed-metal complexes have been made and are discussed. The dimerization constant for the formation of (uranyl citrate)$_2$ was determined potentiometrically and found to agree with the literature values. However, arguments are presented for the necessity of recalculating the values presented in the literature for the equilibrium $UO_2^{2+} + H_3L = UO_2L^- + 3H^+$. The logarithms of the recalculated values are −7.40 for malate, −6.30 for citrate, and −6.85 for tartrate.

Introduction

The formation of mixed-ligand complexes has been extensively studied, and the great amount of quantitative data obtained[3] has made it possible to develop theories regarding the driving forces which bring about the formation of these complexes.[4] However, the formation of mixed-metal complexes (mmc) has not been examined to any significant extent and very little quantitative data are available concerning their formation constants. There have been some studies concerned with the formation of $PtSnCl_4^{4+}$ and other compounds of this type.[5,6] The ability of the hydroxycarboxylic acids to form a mmc has been reported.[7-14] It has been shown that to obtain a mmc the hydroxycarboxylic acid has to contain the basic unit of malic acid.[12] It is also apparent that at least one of the metals involved in the mmc should be capable of forming a polymer when it is involved in complexation with the hydroxycarboxylic acid.

The formation and polymerization of uranyl malate, citrate, and tartrate have been investigated by several workers.[15-21] Basically, the technique used in these studies was potentiometry. The interpretation of the resultant data is, however, controversial. Heitner and Bobtelsky[15] and Li, *et al.*,[17] reported the formaof a mononuclear complex. Feldman, *et al.*,[16,20,21] detected the formation of dimers and higher polymers without finding the mononuclear complex. Furthermore, they showed that the data of Li, *et al.*, could be interpreted in terms of polynuclear complex formation. Rajan and Martell[18,19] restudied this problem using potentiometric titrations and fitted the data in a model which considered a simultaneous equilibrium among the metal ions and mononuclear and polynuclear complexes. The dimerization of the mononuclear complex has also been studied using an extraction technique[13] and considerable differences are present between this work and that done by Martell. In the present study, we attempt to estimate the formation of the uranyl complex with citric acid and the formation of the mmc of uranyl and indium with a malate, tartrate, or citrate.

Experimental Section

Reagents.—Aqueous solutions of citric, D-tartaric (both J. T. Baker analyzed), and DL-malic (Aldrich) acids were prepared from reagent grade materials and standardized potentiometrically. Solutions of indium(III) nitrate or chloride were prepared from metallic In (Fisher, 99.99%) and standardized gravimetrically as the oxide. The uranium stock solution was prepared with $UO_2(NO_3)_2 \cdot 6H_2O$ (Mallinckrodt, CP grade). All the solutions contained 1 *M* KNO_3 (J. T. Baker) which was used to maintain a background ionic strength.

Technique.—The pH was measured with a Corning combined electrode in conjunction with either an Orion Model 801 digital meter or a Radiometer Model 4 meter. The hydrogen ion concentration was calculated by comparison with a standardized HCl solution in 1 *M* KNO_3. During the course of the experiments, nitrogen was continuously passed over the solution to eliminate CO_2 interference. The temperature was kept constant at 25.0 ± 0.05° by water circulated from a thermostated bath.

The infrared spectra were recorded on a Perkin-Elmer Model 221 using sodium chloride plates as cells.

Results and Discussion

Complexation of Uranium(VI) with Citric Acid.—The reactions to be considered are formation of the mononuclear complex

$$UO_2^{2+} + H_3L \rightleftharpoons UO_2L^- + 3H^+$$

$$K_M = \frac{[UO_2L^-][H^+]^3}{[UO_2^{2+}][H_3L]} \qquad (1)$$

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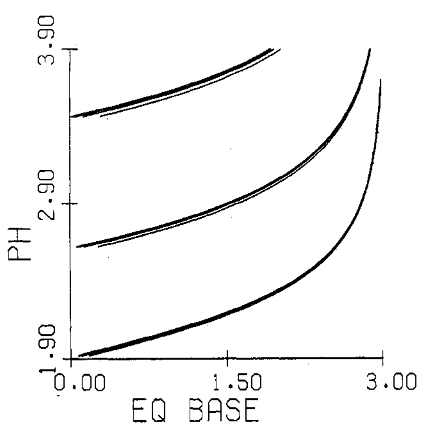

Figure 1.—Computer-simulated titration curves used in determining the possibility of differentiating between mono- and polynuclear complex formation for the uranyl citrate system $[UO_2^{2+}]$: citrate = 1:1. Upper set of curves = 1.61×10^{-4} *M;* middle curves = 1.61×10^{-3} *M;* lower curves = 1.61×10^{-2} *M.* There are four curves in the upper set and three in each of the other two with the upper curve in each set having a K_D of 10^8 and the lowest a K_D of 10^3.

and formation of the binuclear complex

$$2UO_2^{2+} + 2H_3L \rightleftarrows (UO_2L)_2^{2-} + 6H^+$$

$$K_{MD} = \frac{[(UO_2L)_2^{2-}][H^+]^6}{[UO_2^{2+}]^2[H_3L]^2} \qquad (2)$$

These are concentration constants where the hydrogen ion concentration is determined by pH measurements. The dimerization constant can be defined from the above equations as

$$2UO_2L^- \rightleftarrows (UO_2L)_2^{2-}$$

$$K_D = \frac{[(UO_2L)_2^{2-}]}{[UO_2L^-]^2} \qquad (3)$$

In order to assess the possibility of differentiating between mononuclear and polynuclear complex formation, titration curves were simulated by computer calculations for three different concentrations of equimolar mixtures of citric acid with uranyl ion. Figure 1 shows the three sets of curves which were obtained where the upper curve in each set has a K_D of 10^8 and the lowest curve has a value of 10^3. From these curves the following can be concluded. In order to differentiate between a K_D of 10^3 and 10^4 at high concentrations such as 1.61×10^{-2} *M*, the accuracy of the pH measurement should be better than 0.005 pH unit. At 1.61×10^{-4} *M* an accuracy of 0.025 pH unit or better is still required to distinguish a K_D of 10^3 and 10^4. By going to lower concentrations, higher and higher dimerization constants could be distinguished, but it should be pointed out that the curves are almost parallel and a constant shift (uncertainty in the absolute value) in the pH could introduce a large error in the estimation of K_D.

The nondefinitiveness of this method for the simultaneous calculation of K_M and K_{MD} can be seen by looking at the plots of Rajan and Martell.[19] They employed a slope intercept method to determine K_M and K_{MD} where the intercept is equal to K_M. Small changes in the slope yield small changes in K_{MD}, but since the intercept is very close to the origin the value of K_M is uncertain by at least an order of magnitude.

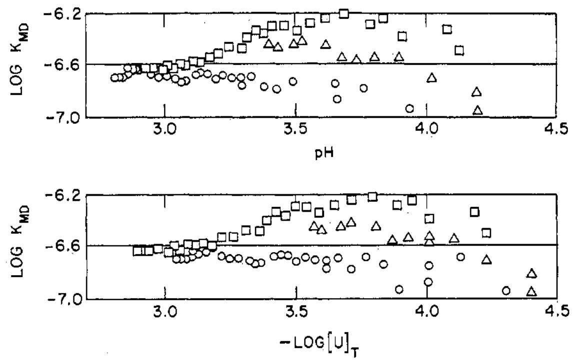

Figure 2.—Log K_{MD} calculated for each data point from three potentiometric titration experiments: □, UO_2:citrate = 2:1; ○, 1:1; △, 1:1 + 1 equiv of base. Straight line represents the average value of log K_{MD} of −6.59.

The simulated titration curves also suggest that the best experimental design is to perform a cross titration by varying the metal and ligand concentrations simultaneously. This is accomplished by adding increasing amounts of a solution containing both uranium and the organic acid to a solution of the supporting electrolyte. Using this method, calibration errors are eliminated since absolute pH values are not required. Furthermore, the measurements are performed in a region where the possibility of differentiating between the constants is maximized.

The uranyl–citrate system was studied in this manner. The initial pH of the solution was adjusted to about 4 to avoid the interference of buffer impurities.[22] Three titrations were performed: one where the titrant contained a U:citrate ratio of 2:1, a second with 1:1, and a third with 1:1 plus the addition of 1 equiv of base. A computer program was written so that a value of K_{MD} could be calculated for each point in the titration. The values of pK for citric acid which were used in the calculation are pK_2 = 2.63, pK_2 = 4.11, and pK_3 = 5.34.[19]

Figure 2 shows a plot of the values for log K_{MD} calculated for each point in the titration and plotted as ordinate against either pH or −log (total uranium). The value of −6.59 obtained for log K_{MD} by averaging the experimental results from the three potentiometric experiments is shown as a solid line. From these plots it can be seen that there is no overall trend in the value of K_{MD} with changes in either the uranium concentrarion or pH. The average values obtained from each titration are −6.44 for the experiment with a 2:1 ratio, −6.74 for the 1:1 ratio, and −6.57 for the 1:1 ratio with 1 equiv of base added.

The value obtained for K_{MD} is compared with the published values in Table I and the agreement appears to be very good. We can assume, therefore, that the values reported for K_{MD} for tartrate and malate (also shown in Table I) are valid.

As we have stated, the values given in the literature for K_M are not reliable. However, good values can be calculated by utilizing measurements of K_D. The extraction of U(VI)[13] from aqueous solutions of malic, tartaric, and citric acids into a benzene solution of then-

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TABLE I

SUMMARY OF FORMATION CONSTANTS

	Log K_M				Log K_{MD}				Log K_D		Log K_{mmc}
	18, 19	17	15	Recalcd	18, 19	16	17	This work	18, 19	13	This work
Malate	−5.55			−7.40	−7.75	−7.86			3.35	7.0	−7.62
Tartrate	−5.62			−6.85	−8.00	−8.02			3.24	5.7	−7.14
Citrate	−5.21	−4.4	−8.4	−6.30	−6.61	−6.64	−6.56	−6.59	3.96	6.0	−11.58

oyltrifluoroacetone was studied at pH 4 over the concentration range of 5×10^{-8} to 3×10^{-3} *M* uranyl ion. By using a large excess of ligand, the presence of the free uranyl ion was essentially eliminated. The results were very conclusive and yielded the values for K_D shown in Table I.[13] Not surprisingly, these differ significantly from the values calculated with the data of Martell. Using the numbers for K_D obtained from the solvent extraction experiments and the literature values for K_{MD}, the values of K_M may be computed using eq 3 and these are shown in the table as log K_M recalculated. Again they differ significantly from the uncertain values given in the literature.

Mixed-Metal Complex Formation of In(III) and U(VI) with Some Hydroxycarboxylic Acids.—The composition of the mmc of In(III) and U(VI) and of In(III) and Cr(III) has already been studied.[12,13] It was concluded that the composition of the complex is MM′L$_2$. In the case of citric acid four protons are liberated from each molecule, but only three from tartaric and malic acids. It was also observed that the formation of the mmc was accompanied by spectral changes in the visible region.

It is now possible to perform potentiometric titrations in order to determine the value for K_{mmc} which in the case of citric acid is defined as

$$UO_2^{2+} + In^{3+} + 2H_4L \rightleftarrows UO_2InL_2^{3-} + 8H^+ \qquad (4)$$

Two of the protons come from the hydroxy groups. In the case of malic and tartaric acids the equilibrium is

$$UO_2^{2+} + In^{3+} + 2H_3L \rightleftarrows UO_2InL_2^{-} + 6H^+ \qquad (5)$$

A potentiometric titration was performed for each of the hydroxycarboxylic acids under conditions where U:In:H$_n$L is 1:1:2. In a given experiment a value of K_{mmc} was calculated for each point in the titration. It was, of course, necessary to account for the amount of uranium present as UO_2L^- and $(UO_2L)_2^{2-}$ utilizing the values of K_M given in references 18 and 19 and the values for K_D given in reference 13. Under the conditions used in these experiments, it was found that indium is not significantly complexed by the acids. This is clearly illustrated by the fact that In(OH)$_3$ precipitates when a titration is performed in the absence of uranium but in the presence of the hydroxycarboxylic acid. No precipitate is found when uranium is present due to the formation of the mmc. The calculated values of K_{mmc} for malic, citric, or tartaric show no trends with either pH or metal concentrations. As an example, the data for malic acid are shown in Figure 3 as a plot of K_{mmc} *vs.* both pH and −log [U]$_T$. The average value is shown as the solid line and the constants for all three acid systems are given in Table I.

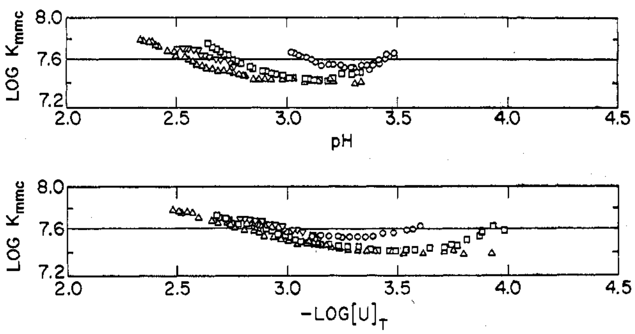


Figure 3.—Log K_{mmc} calculated for the interaction among In(III), U(VI), and malic acid from each data point obtained from four potentiometric titration experiments: △, In:UO$_2$: malate = 1:1:2; ▽, 1:1:2; □, 1:1:2 + 1.5 equiv of base; ○, 1:1:2 + 2 equiv of base. Straight line represents the average value of log K_{mmc} of −7.62.

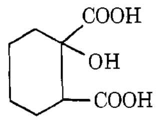
Direct comparison of the values for K_{MD} and K_{mmc} for malate and tartrate can be made and as you might expect the formation constant for the mixed-metal complex is greater than the dimerization constant. A stabilization of approximately 1 order of magnitude is observed in the case of tartrate. A straightforward comparison in the case of citrate cannot be made because of the difference in the number of protons involved.

In a recent article[14] Binder has utilized spectrophotometric measurements to study the formation of a mixed-metal complex involving Sn(II), Fe(III), and citric acid. The equilibrium which he observed to be taking place can be written as

$$Sn^{2+} + Fe^{3+} + 3H_4L = SnFeL(HL)_2^{5-} + 10H^+$$

to be consistent with the nomenclature employed in this work. This equilibrium differs from the uranium–indium case by involving an additional citric acid but utilizing only one instead of two protons from the hydroxy groups. The value of the equilibrium constant for the above reaction is log K_{mmc} = −17.83. Because of the above stated differences a comparison cannot easily be made with the uranium–indium system. Binder also studied the mixed-valent system Fe(II)–Fe(III), with citric acid, but unfortunately was unable to obtain a formation constant.

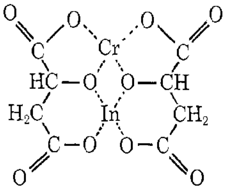
The structural requirements necessary for a ligand to be able to give a mmc has been extensively studied and it is clear that the basic structure of malic acid is required.[12,13] No cyclic acids had yet been studied so we prepared 1-hydroxy-1,2-cyclohexanedicarboxylic acid (CHDH). This compound contains the



structure of malic acid and has similar acidic properties (pK_1 = 3.49 and pK_2 = 5.48).

However, in solvent extraction experiments performed in the same manner as before,[12] no evidence was found for a mmc between U(VI) and In(III) with CHDH. Recently, the structures of *cis*- and *trans*-1,2-cyclohexanedicarboxylic acids were published.[23,24] A model of this compound was constructed and one of the hydrogens interchanged with a hydroxyl group. If the OH is in an equatorial position the structure is similar to those found for citric acid.[25] But if the hydroxyl group is in an axial position, the conditions for obtaining a tridentate chelate are not fulfilled. Since CHDH does not form a mmc then the hydroxyl group is probably in the axial position. Additional supporting evidence is the low complexing power of this acid with the uranyl ion. A value of only −8.63 was found for log K_M.[26]

Infrared Investigation of the Mixed-Metal Complex.—Newman, *et al.*,[12,13] have proposed the following structure for the mmc



Attempts to prepare the solid uranium–indium complex in a crystalline form failed. Techniques such as salting out, concentrating, cooling, and solvent addition were all attempted. However, it was found possible to extract the pure mmc into an ether solution of trilaurylamine (TLA). The ether and any accompanying water were removed by evaporation. Then the ir spectra of the TLA extract were recorded and compared with those of the organic acids, amine salts of the acids, and TLA extracts of uranyl citrate and uranyl malate. From the spectra of the uranyl citrate extracted with trilaurylamine and bis(trilaurylamine) citrate, it can be concluded that only some of the carboxyl groups participate in the complex formation. The spectra show a band at 1730 cm^{-1} due to the stretching vibration of the undissociated carboxyl group. The band assigned to the asymmetric vibration of the ionized carboxyl group is split in two (1620 cm^{-1} and 1570–1580 cm^{-1}). This can be explained by the existence of carboxyl groups bound in two different ways. A melt of bis(trilaurylamine) citrate was prepared and found to exhibit a band at ~3400 cm^{-1} (appears as a shoulder to the CH_2 stretching mode). This effect is a result of the coordination of the hydroxyl group to the uranyl ion and possible hydrogen bonding to a neighboring C=O group or amine.

The shift of a stretching band to lower frequencies usually causes a shift of the corresponding bending bands to higher frequencies.[27] As expected, the spectrum of uranyl citrate in TLA in the region due to the bending vibrations of the hydroxyl group would be moved to higher frequencies. This is indeed what is observed.

Bis(trilaurylamine) citrate	Uranyl citrate in TLA
1290	1305
1190	1210
1110	1115, 1080(?)

Furthermore, this is evidence that the hydroxylic acid group is present and participating in the coordination of the monomer. These findings are supported by Martell's[19] ir measurements using D_2O solutions which showed that after 3 equiv of base was added the three carboxylic acids are the main proton suppliers, and not the hydroxyl group.

The spectra of the extracted $UO_2In(citrate)_2$ shows the same splitting of the asymmetric vibrations due to the dissociated carboxyl group but the bending vibrations due to the hydroxyl groups become very weak shoulders. The stretching vibrations due to the hydroxyl group in the region 3500–3000 cm^{-1} are not present. This demonstrates the loss of the hydroxyl proton during the mmc formation, supporting the observation from the potentiometric data that 4 equiv of acid is released.

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