Asian Jorunal of Chemistry Vol. 8, No. 1 (1996), 75–84

Formation of Mixed Ligand Complexes of UO_2^{2+} Involving Some Nitrogen and Oxygen Donor Ligands

MAMTA SINGH and RAM NAYAN*
Department of Chemistry
Hindu College, Moradabad-244 001, India

The complexation reactions of UO_2^{2+} ion with nitrogen and oxygen donor ligands, 1-amino-2-naphthol-4-sulphonic acid, *o*-aminophenol (ap), 2-hydroxybenzoic acid (sa), 3-carboxy-4-hydroxybenzenesulphonic acid (ss) and 1,2-dihydroxybenzene (ca) have been investigated in aqueous solution employing the pH-titration technique. Aanalysis of the experimental data recorded at 25°C and at an ionic strength of 0.10 M KNO_3 indicates formation of binary, hydroxo and ternary complexes including $UO_2(an)$, $UO_2(an)_2^{2-}$, $UO_2(an)(OH)^-$, $UO_2(ap)^+$, $UO_2(ap)_2$, $UO_2(sa)$, $UO_2(sa)_2^{2-}$, $UO_2(sa)(OH)^-$, $UO_2(sa)_2(OH)^{3-}$, $UO_2(ss)$, $UO(ss)_2^{4-}$, $UO(ss)(OH)^{2-}$, $UO_2(ss)_2(OH)^{5-}$, $UO_2(ca)$, $UO_2(ca)_2^{2-}$, $UO_2(ca)(OH)^-$, $UO_2(an)(ap)^-$, $UO_2(an)(sa)^{2-}$, $UO_2(an)(ss)^{3-}$, $UO_2(an)(ca)^{2-}$, $UO_2(ap)(sa)^-$, $UO_2(ap)(ss)^{2-}$, $UO_2(ap)(ca)^-$, $UO_2(sa)(ss)^{3-}$, $UO_2(sa)(ca)^{2-}$, and $UO_2(ss)(ca)^{3-}$ in mixtures containing corresponding metal-ligand pair of ligand ratio. Formation constant values of the existing species have been evaluated and the results have been discussed.

INTRODUCTION

Interesting and major results have been reported on coordination chemistry of nitrogen and oxygen donor ligands. These ligands have been widely used in kinetic studies[1, 2], and many analytical methods based on complex formation reactions in solution[3,4]. Problems related to equilibrium measurements have been solved by means of various experimental techniques[5–10] and methods of evaluation of equilibrium constant. Besides the investigation of complex equilibria and the kinetics of complex formation, an increasing number of other studies also are currently devoted to problems of structure, bonding and electronic structures making extensive use of modern methods of structural analysis such as infrared spectrometry, magnetic susceptibility measurements, nuclear magnetic resonance and Mössbauer spectroscopy[11–15].

In spite of the extremely rapid development of coordination chemistry, the equilibrium studies on nitrogen and oxygen donor molecules with the metal ions involving the formation of mononuclear complex species have not as yet reached maturity. Such complexes have a potential for further developments. A knowledge of mononuclear species provides an important tool in the investigation of other complicated complex species including mixed ligand complexes existing in solution. Thus, in the present communication a systematic study on the complex-formation between UO_2^{2+} ion and nitrogen and oxygen donor ligands, 1-amino-2-naphthol-4-sulphonic acid (an), *o*-aminophenol (ap), 2-hydroxybenzoic acid (salicylic acid, sa), 3-carboxy-4-hydroxybenzene sulphonic acid (5-sulphosalicylic acid, ss), 1,2-dihydroxybenzene (catechol, ca) has been carried out using pH-titration technique.

EXPERIMENTAL

Carbon dioxide free solution was prepared by dissolving 50 g of potassium hydroxide (A.R.) in 50 cm^3 distilled water in pyrex flask. A suitable volume of potassium hydroxide solution was diluted and standardized by titrating with 0.2 N oxalic acid solution. A stock solution of 0.2150 N potassium hydroxide was thus obtained. Standard solutions of 1.0 M potassium nitrate and 0.0387 N HNO_3 were prepared using analytical grade reagents. Aqueous solution (5.0×10^{-3} M) of uranyl nitrate (Loba, G.R.) was prepared. UO_2^{2+} content was determined by oxine method[16]. Aqueous, solutions (5.0×10^{-3} M) of each 3-carboxy-4-hydroxybenzenesulphonic acid (CDH) and 1,2-dihydroxybenzene (BDH) were prepared by direct weighing. Compounds 1-amino-2-naphthol-4-sulphonic acid (CDH) and *o*-aminophenol (Loba) were purified by dissolving in aqueous alkali medium and reprecipitating by dilute HCl. Monosodium salt solution of 1-amino-2-naphthol-4-sulphonic acid (5.0×10^{-3} M) was obtained by adding required alkali solution.

2-Hydroxybenzoic acid (B.D.H.) and *o*-aminophenol were dissolved in known amount of alkali and the volume was raised to get 5.0×10^{-3} M concentration of each ligand. The excess of alkali present in titration mixtures of these ligands was neutralized by adding known amount of nitric acid solution before titration.

Procedure

A number of mixtures (i) HNO_3, (ii) 5.0×10^{-4} M ligand + (i), (iii) 5.0×10^{-4} M metal nitrate + (ii), (iv) 2.5×10^{-4} M metal nitrate + (ii), were prepared for studying the equilibrium reactions involving proton-ligand dissociation and simple complex formation. Similarly, for the mixed ligand complex, UO_2^{2+}-AB (where A, B are possible pairs of ligands an^- , ap, sa, ss and ca), the mixtures containing UO_2^{2+}, A, B in 1 : 1 : 1 ratio (each 5.0×10^{-4} M) + (i) were prepared and titrated. Experiments were carried out, in an inert atmosphere of nitrogen gas by bubbling oxygen-free nitrogen gas through the solution in the titrating vessel keeping the initial volume of each mixture 50 cm^3, at an ionic strength of 0.10 M KNO_3 and temperature 25°C. The pH-metric titrations were continued to a pH of *ca.* 11.00.

From the experimental data pH vs volume of alkali curves were plotted and were utilized to calculate moles of alkali used per mole of metal/ligand (a) at different pH.[17] Further, 'a' values were plotted against pH and the existing complex equilibria were analysed. A scientific calculator Casio fx-910 was used for calculation work.

RESULTS AND DISCUSSION

Proton-ligand dissociation constants

The titration curve of an^- lies between $a = -1$ and 1 in the pH range 3.0–11.0 (Fig.1). A sharp inflection in the curve at $a = 0$ indicates that two protons are

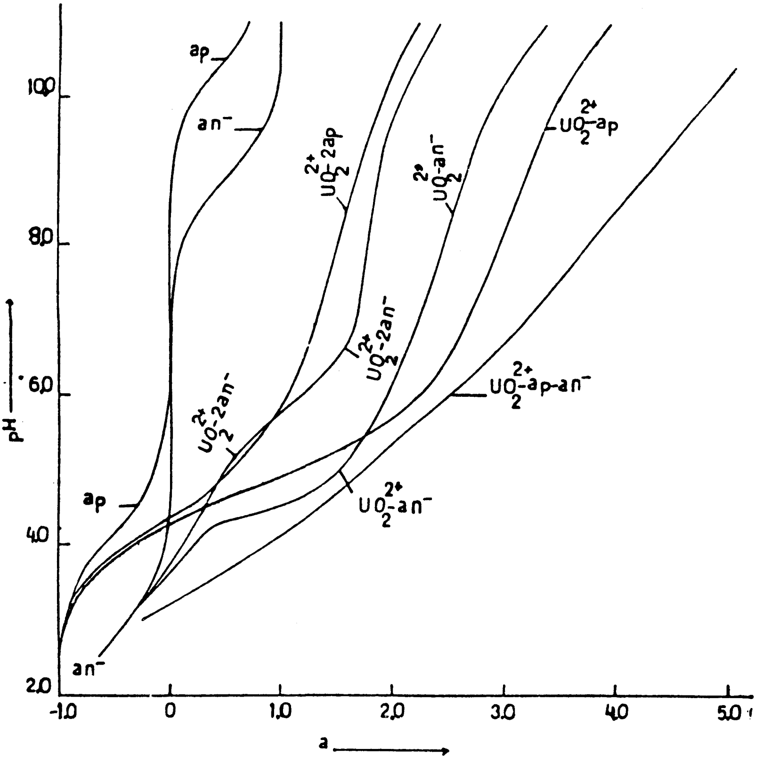

Fig. 1. pH vs. 'a' curves for UO_2^{2+} complexes with an^- and ap

liberated in steps, respectively, from protonated amino group and the phenolic group. The stepwise proton dissociation constants are $K_1^H = 10^{-2.79 \pm 0.02}$ and $K_2^H = 10^{-8.85 \pm 0.04}$. At low pH values, the colour of the ligand is red. A gradual colour change from red to orange takes place between pH 2.50 and 4.69 (below a = 0) due to the deprotonation of the protonated ligand. A steep inflection in the titration curve at a = 0 confirms that the neutral ligand molecule is orange. Further, colour change (light brown) appears at pH *ca.* 6.45. The intensity of brown colour gradually increases with the increase in anionic ligand concentration up to pH *ca.* 10.0, where the value of a is 1.0 (Fig. 1).

Dissociation of two protons, in steps, from protonated amino group and the phenolic group in *o*-aminophenol system has also been inferred. A gradual colour change in the mixture, from brown to yellow and finally to yellowish-green at higher pH values has been noted. The colour change may be expected due to existence of protonated, neutral and anionic ligands, respectively. The corresponding proton-ligand dissociation constants ($K_1^H = 10^{-4.18 \pm 0.03}$ and $K_2^H = 10^{-10.53 \pm 0.02}$) were evaluated as described earlier.

A sharp inflection in pH *vs* 'a' curve of sa system shows that protons from the —COOH and —OH groups are dissociated in two distinct steps above pH *ca.* 2.4 (below pH *ca.* 4.6) and 11.8, respectively. The titration mixture, however, remains colourless throughout the titration. The calculated proton-ligand dissociation constants are: $K_1^H = 10^{-2.91 \pm 0.01}$, $K_2^H = 10^{-13.50 \pm 0.02}$.

The proton of —SO_3H group in ss system is dissociated at very low pH value and the ligand mixture remains colourless under the experimental range of pH. The steep inflection in the titration curve at a = 2 shows that the two proton-ligand dissociation equilibria corresponding to proton dissociation from —COOH and –OH groups exist independently. The proton-ligand dissociation constant values for these steps are: $K_2^H = 10^{-2.36 \pm 0.07}$ and $K_3^H = 10^{-11.52 \pm 0.03}$. The higher value of dissociation constant for the phenolic group than that of sa is probably due to electron withdrawning nature of —SO_3H group.

Proton-ligand equilibria, corresponding to dissociation of protons from the two phenolic groups of ca, is evident from the titration curve. The dark reddish brown colour of the neutral ligand molecule gradually turns into yellowish brown (at pH *ca.* 8.6), and subsequently the mixture appears light reddish brown beyond pH *ca.* 10.0. Proton-ligand dissociation constants, $K_1^H = 10^{-9.40 \pm 0.03}$ and $K_2^H = 10^{-11.58 \pm 0.02}$ evaluated as earlier can be compared with those of Martell *et al.*[18].

Binary complexes

1:1 *Metal-ligand system*: Formation of $UO_2(an)$ is indicated by 1:1, metal-an^- titration curve (Fig. 1). The colour of the complex is orange. Between pH *ca.* 4.51 (a = 1.0) and 5.34, the colour of the solution changes to yellowish brown with increase in pH values. Beyond pH *ca.* 5.34 the reaction mixture appears turbid, and the intensity of the turbidity and its colour gradually increases up to pH 11.0. The equilibrium constants of $UO_2(an)$ and $UO_2(an)(OH)^-$ species (Table-1) were calculated as described earlier[17]. The complex species $UO_2(ap)^+$ is formed below pH *ca.* 4.90. But, unlike an^- system the monohydroxo complex $UO_2(ap)(OH)$ does not exist in solution as the reaction mixture remains in turbid form (yellowish brown) above pH *ca.* 4.79. A comparison of pH *vs.* 'a' curves of sa and 1 : 1, metal-sa system, and an observation on the colour of reaction mixture show that a light yellow colour $UO_2(sa)$ complex is formed, below pH *ca.* 4.54 (a = 2.0). Further, between a = 2.0 and 3.0, formation of soluble and anionic species $UO_2(sa)(OH)^-$ is indicated. The titration mixture becomes turbid (yellow) from pH *ca.* 5.58. Formation of $UO_2(ss)^-$ and $UO_2(ss)(OH)^{2-}$ is also evident below pH *ca.* 5.60 (a = 4.0) from a colour change identical to sa system and pH *vs.* 'a' curve of corresponding system. The 1:1, UO_2^{2+}-ss mixture remains in turbid form (yellow) beyond pH *ca.* 5.6. Formation of 1:1 metal-ca complex is indicated below pH *ca.* 5.57 (a = 2.0). Between a = 2 and 3 (pH *ca.* 8.63), UO_2-$(ca)(OH)^-$ association takes place in the mixture which turns turbid at pH *ca.* 6.53 (a = 2.53).

1:2, *Metal-ligand system:* 1:2 UO_2^{2+}-an^- mixture turns into a light yellow turbid form at pH *ca.* 5.80, and the amount of turbidity further increases. Comparison of curves of 1:2 metal-ligand system with that of composite curve obtained from 1:1, metal-an^- and ligand titrations indicates that the equilibrium involving $UO_2(an)_2^{2-}$ exists in solution below pH *ca.* 5.75. Similarly metal-ap mixture also remains turbid above pH *ca.* 4.74. However, the neutral complex species $UO_2\text{-}(ap)_2$ is formed below a = 1.0 (pH *ca.* 5.81). It has also been observed that the change in amount of turbidity is comparable with that of an^- complex system. The calculated equilibrium constant is given in Table-1. The pH *vs.* 'a' curves for 1:2 metal-oxygen donor ligands (sa and ss) show that $UO_2(sa)_2^{2-}$ and $UO_2(ss)_2^{4-}$ exist below pH *ca.* 4.65 (a = 2.0) and 5.40 (a = 3.0), respectively. Further, formation of $UO_2(sa)_2(OH)^{3-}$, $UO_2(ss)_2(OH)^{5-}$ is indicated between a = 2.0 and 2.5, 3.0 and 3.5, respectively. The titration curve for sa complex system shows a steep inflection at a = 3.0. A similar inflection also occurs in the ss system after the formation of monohydroxo complex (at a = 3.5). The reaction mixtures of sa and ss containing metal turn turbid at pH *ca.* 5.9 and 6.2, respectively. Only nonprotonated and monohydroxo complexes, in each system, exist in solution. The pH *vs.* 'a' curve for ca system shows a weak inflection at a = 1.0 (pH *ca.* 5.22) and a steep inflection at a = 2.0 (pH *ca.* 7.90) indicating the formation of $UO_2(ca)$ and $UO_2(ca)_2^{2-}$ in two distinct steps. There is a large difference in K_1 and K_2 values (the corresponding values in other systems are either almost identical or show a very small difference). Beyond pH *ca.* 7.26 the reaction mixture being in turbid form did not permit any calculation.

TABLE-1

EQUILIBRIUM CONSTANTS OF BINARY AND HYDROXY COMPLEXES OF UO_2^{2+} with an^-, ap, sa, ss and ca (25°C, $\mu = 0.10$ M KNO_3)

Reaction		log K
$UO_2^{2+} + an^{2-}$	$\rightleftarrows UO_2(an)$	7.85 ± 0.11
$UO_2(an) + an^{2-}$	$\rightleftarrows UO_2(an)_2^{2-}$	7.11 ± 0.02
$UO_2(an) + OH^-$	$\rightleftarrows UO_2(an)(OH)^-$	9.10
$UO_2^{2+} + ap^-$	$\rightleftarrows UO_2(ap)^+$	9.79 ± 0.08
$UO_2(ap)^+ + ap^-$	$\rightleftarrows UO_2(ap)_2$	9.05 ± 0.05
$UO_2^{2+} + sa^{2-}$	$\rightleftarrows UO_2(sa)$	13.50 ± 0.25
$UO_2(sa) + sa^{2-}$	$\rightleftarrows UO_2(sa)_2^{2-}$	12.95 ± 0.43
$UO_2(sa) + OH^-$	$\rightleftarrows UO_2(sa)(OH)^-$	8.99
$UO_2(sa)_2^{2-} + OH^-$	$\rightleftarrows UO_2(sa)_2(OH)^{3-}$	9.05
$UO_2^{2+} + ss^{3-}$	$\rightleftarrows UO_2(ss)^-$	11.17 ± 0.22
$UO_2(ss)^- + ss^{3-}$	$\rightleftarrows UO_2(ss)_2^{4-}$	10.53 ± 0.18
$UO_2(ss)^- + OH^-$	$\rightleftarrows UO_2(ss)(OH)^{2-}$	8.78
$UO_2(ss)_2^{4-} + OH^-$	$\rightleftarrows UO_2(ss)_2(OH)^{5-}$	8.25
$UO_2^{2+} + ca^{2-}$	$\rightleftarrows UO_2(ca)$	15.41 ± 0.04
$UO_2(ca) + ca^{2-}$	$\rightleftarrows UO_2(ca)_2^{2-}$	12.76 ± 0.05
$UO_2(ca) + OH^-$	$\rightleftarrows UO_2(ca)(OH)^-$	7.55

Comparing the values of equilibrium constants (Table-1) it is concluded that the complexing tendency of the ligands follows the order: ca > sa > ss > ap > an.

The oxygen donors, ca, sa and ss, behave as stronger electron donor ligands than the nitrogen-oxygen mixed donor ligands, ap and an. A large size of an may be considered the cause of its lowest electron-donating capability.

The order of stability constant for coordination of OH^- ion with 1:1, metal-ligand complexes: $UO_2(an) > UO_2(sa) \approx UO_2(ss)^- > UO_2(ca)$ can be explained on the basis of electron density around the central atom in the non-protonated complex species. In 1:2, metal-ligand complexes OH^- ion attachment follows a reverse order: $UO_2(sa)_2^{2-} > UO_2(ss)_2^{4-}$. The low value in case of $UO_2(ss)_2^{4-}$ system is probably due to larger repulsion between OH^- ion and highly charged anionic complex as well as the steric hindrance.

Mixed ligand complexes

A gradual colour change (mixed ligand complex systems) in mixtures of ca with sa, ss (from brownish yellow to light yellow, brownish yellow to light canary yellow, between pH *ca.* 2.40 and 4.85, 2.40 and 4.17, respectively), an^- with sa, ss, ca (from brownish red to dark red, red to orange, brownish red to yellow, between pH *ca.* 2.42 and 3.35, 2.42 and 5.36, 2.42 and 5.16, respectively) and ap with ss, sa, ca, an^- (from orange to yellow, yellowish orange to greenish black, light orange to green, dark red to dark brown, between pH *ca.* 2.40 and 3.85, 2.42 and 4.69, 2.50 and 4.20, 2.42 and 4.45, respectively) has been noted. The UO_2^{2+}-sa-ss mixture is colourless in the pH range of mixed ligand complex formation in solution. All the mixtures of UO_2^{2+} with the pair of ligands an^--ap, an^--sa, an^--ss, an^--ca, ap-sa, ap-ss, ap-ca, sa-ss, sa-ca and ss-ca appear turbid above pH 5.83, 5.58, 5.55, 5.53, 5.65, 4.55, 6.03, 6.56, 5.80 and 5.58, respectively. Existence of turbidity did not permit further analysis.

On comparing the pH *vs.* 'a' curves of each mixed system with the coresponding ligands, 1:1 and 1:2 metal-ligand systems, it has been concluded that MAB type complex is formed in solution containing the metal ion and ligand pair in 1:1:1 ratio. In some cases the mixed ligand comples formation is supported by a colour change discussed above in the mixture.

$$M + A + B \rightleftarrows MAB; \quad K = \frac{[MAB]}{[M][A][B]}$$

Considering the existence of free M, MA, MA_2, MB, MB_2 and MAB in solution, [A] was calculated by Newton's methods using equations as described earlier[17,19]

$$P_1[A]^3 + P_2[A]^2 + P_3[A] - P_4 = 0$$

[A] value was further utilized to obtain [B], [M] and [MAB] as below:

$$[B] = \frac{C_M(n + l - a)}{b_l} - \frac{a_l\,[A]}{b_l}$$

$$= e - d[A] \qquad (1)$$

(n/*l*= 1, 2 and 3 for nn, ap, an, ca, sa and ss respectively)

$$[M] = \frac{a_2[A]}{1 + K_{1B}[B] + K_{1B}K_{2B}[B]^2 - K_{1A}K_{2A}[A]^2} \tag{2}$$

$$= \frac{b_2[B]}{1 + K_{1A}[A] + K_{1A}K_{2A}[A]^2 - K_{1B}K_{2B}[B]^2}$$

$$[MAB] = C_M - [MA] - [MA_2] - [MB] - [MB_2] - [M] \tag{3}$$

where

$$P_1 = K_{1A}K_{2A}(a_2 - b_2d) + K_{1B}K_{2B}(b_2d^3 - a_2d^2)$$

$$P_2 = K_{1A}K_{2A}b_2e + K_{1B}K_{2B}(2a_2ed - 3b_2ed^2) + K_{1A}a_2 - K_{1B}b_2d^2$$

$$P_3 = K_{1B}K_{2B}e^2(3b_2d - a_2) + 2K_{1B}db_2e + a_2 + b_2d$$

$$P_4 = b_2e + K_{1B}b_2e^2 + K_{1B}K_{2B}b_2e^3$$

$$a_1 = \frac{n[H^+]^n}{K^H_{1A}K^H_{2A}K^H_{3A}\ldots K^H_{nA}} + \frac{(n-1)\,[H^+]^{n-1}}{K^H_{2A}K^H_{3A}\ldots K^H_{nA}} + \ldots + \frac{[H^+]}{K^H_{nA}}$$

$$a_2 = \frac{[H^+]^n}{K^H_{1A}K^H_{2A}K^H_{3A}\ldots K^H_{nA}} + \frac{[H^+]^{n-1}}{K^H_{2A}K^H_{3A}\ldots K^H_{nA}} + \ldots + \frac{[H^+]}{K^H_{nA}} + 1$$

$$b_1 = \frac{l[H^+]^l}{K^H_{1B}K^H_{2B}K^H_{3b}\ldots K^H_{lB}} + \frac{(l-1)[H^+]^{l-1}}{K^H_{2B}K^H_{3B}\ldots K^H_{lB}} + \ldots + \frac{[H^+]}{K^H_{lB}}$$

$$b_2 = \frac{[H^+]^l}{K^H_{1B}K^H_{2B}K^H_{3B}\ldots K^H_{lB}} + \frac{[H^+]^{l-1}}{K^H_{2B}K^H_{3B}\ldots K^H_{lB}} + \ldots + \frac{[H^+]}{K^H_{lB}} + 1$$

$$e = \frac{C_M(n + 1 - a)}{b_1}$$

$$d = \frac{a_1}{b_1}$$

The values of equilibrium constants are reported in Table-2.

Formation constant value for the addition of ss to 1 : 1, UO_2^{2+} complex with sa is almost comparable in magnitude with the values for the aqua-ion. A parallel effect is noted on addition of sa to 1 : 1, UO_2^{2+}-ss complex. These informations are in agreement with those of Perrin and coworkers[20] reported earlier on ternary complexes of some biologically important ligands, ethylenediamine, histamine, serine and salicylic and salicylic acid with Cu^{2+}. But, for the reaction $CuA^{2+} + B \rightleftarrows CuAB$ (where A = 2,2′-bipyridyl and B is the anion of salicylic acid, catechol or tiron), Martell *et al.*[18] reported higher values of the stepwise formation constants (from 0.9 to 1.5 logarithm units) than for the addition of B to the hydrated Cu^{2+} ion. Earlier findings[19, 21] on mixed ligand complexes of adenine, xanthine and hypoxanthine involving tripositive rare earth ions can also be compared with the latter results. In all the remaining systems, studied here, formation constants for addition of one of the ligands to 1 : 1 metal complex with the other ligands are higher (from 0.89 to 3.33 logarithm units) than K_1 values for the addition of the ligand to aqua-ion.

TABLE-2

EQUILIBRIUM CONSTANTS OF TERNARY COMPLEXES OF UO_2^{2+} WITH POSSIBLE PAIRS OF an^-, ap, sa, ss and ca (25°C, $\mu = 0.10$ M KNO_3)

Reaction	log K
$UO_2^{2+} + an^{2-} + ap^- \rightleftarrows UO_2(an)(ap)^-$	19.07 ± 0.37
$UO_2(an) + ap^- \rightleftarrows UO_2(an)(ap)^-$	11.22
$UO_2(ap)^+ + an^{2-} \rightleftarrows UO_2(an)(ap)^-$	9.28
$UO_2^{2+} + an^{2-} + sa^{2-} \rightleftarrows UO_2(an)(sa)^{2-}$	22.41 ± 0.36
$UO_2(an) + sa^{2-} \rightleftarrows UO_2(an)(sa)^{2-}$	14.56
$UO_2(sa) + an^{2-} \rightleftarrows UO_2(an)(sa)^{2-}$	8.91
$UO_2^{2+} + an^{2-} + ss^{3-} \rightleftarrows UO_2(an)(ss)^{3-}$	20.06 ± 0.31
$UO_2(an) + ss^{3-} \rightleftarrows UO_2(an)(ss)^{3-}$	12.21
$UO_2(ss)^- + an^{2-} \rightleftarrows UO_2(an)(ss)^{3-}$	8.89
$UO_2^{2+} + an^{2-} + ca^{2-} \rightleftarrows UO_2(an)(ca)^{2-}$	23.74 ± 0.07
$UO_2(an) + ca^{2-} \rightleftarrows UO_2(an)(ca)^{2-}$	15.89
$UO_2(ca) + an^{2-} \rightleftarrows UO_2(an)(ca)^{2-}$	8.33
$UO_2^{2+} + ap^- + sa^{2-} \rightleftarrows UO_2(ap)(sa)^-$	26.62 ± 0.27
$UO_2(ap)^+ + sa^{2-} \rightleftarrows UO_2(ap)(sa)^-$	16.83
$UO_2(sa) + ap^- \rightleftarrows UO_2(ap)(sa)^-$	13.12
$UO_2^{2+} + ap^- + ss^{3-} \rightleftarrows UO_2(ap)(ss)^{2-}$	23.63 ± 0.40
$UO_2(ap)^+ + ss^{3-} \rightleftarrows UO_2(ap)(ss)^{2-}$	13.84
$UO_2(ss)^- + ap^- \rightleftarrows UO_2(ap)(ss)^{2-}$	12.46
$UO_2^{2+} + ap^- + ca^{2-} \rightleftarrows UO_2(ap)(ca)^-$	23.22 ± 0.13
$UO_2(ap)^+ + ca^{2-} \rightleftarrows UO_2(ap)(ca)^-$	13.43
$UO_2(ca) + ap^- \rightleftarrows UO_2(ap)(ca)^-$	7.81
$UO_2^{2+} + sa^{2-} + ss^{3-} \rightleftarrows UO_2(sa)(ss)^{3-}$	25.18 ± 0.16
$UO_2(sa) + ss^{3-} \rightleftarrows UO_2(sa)(ss)^{3-}$	11.68
$UO_2(ss)^- + sa^{2-} \rightleftarrows UO_2(sa)(ss)^{3-}$	14.01
$UO_2^{2+} + sa^{2-} + ca^{2-} \rightleftarrows UO_2(sa)(ca)^{2-}$	30.89 ± 0.61
$UO_2(sa) + ca^{2-} \rightleftarrows UO_2(sa)(ca)^{2-}$	17.39
$UO_2(ca) + sa^{2-} \rightleftarrows UO_2(sa)(ca)^{2-}$	15.48
$UO_2^{2+} + ss^{3-} + ca^{2-} \rightleftarrows UO_2(ss)(ca)^{3-}$	27.70 ± 0.56
$UO_2(ss)^- + ca^{2-} \rightleftarrows UO_2(ss)(ca)^{3-}$	16.53
$UO_2(ca) + ss^{3-} \rightleftarrows UO_2(ss)(ca)^{3-}$	12.29

From the distribution curves (Fig. 2—M-ap-an system) plotted between the percentage of the metal ion present in different species and pH, it has been inferred

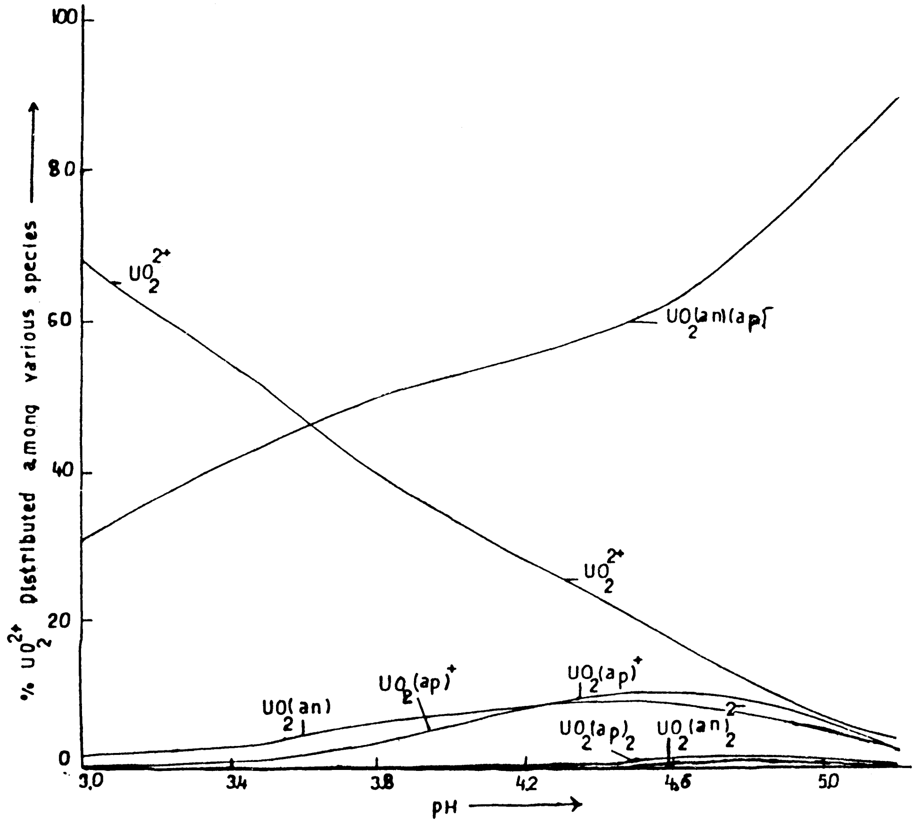

Fig. 2. Percentage of metal ions distributed among various species with pH in 1 : 1 : 1 UO_2^{2+}-an$^-$-ap mixture

that the amount of free metal decreases with the increase of pH in all the mixed ligand complex systems. In case of ap-ca mixture the amount of free UO_2^{2+} remains nearly negligible from the initial pH of ternary complex formation. The percentage of free metal, mixed ligand species formed in solution containing 1 : 1: 1, metal and ligand pairs, ap-ca, ap-sa, ap-ss, ap-an, ca-sa, ca-ss, ca-an, sa-ss, sa-an and ss-an, mixtures are: 0.42, 8.40; 8.66, 88.98; 7.50, 88.23; 4.0, 90; 30.90, 32.92; 24.15, 8.94; 34.51, 26.21; 3.76, 87.06; 6.45, 81.21 and 7.18, 83.31 respectively just before the pH of precipitation of the titration mixture

ACKNOWLEDGEMENTS

Authors are thankful to the U.G.C., New Delhi for financial assistance.

REFERENCES

1. A.C. Dash and B. Mohanty, *J. Inorg. Nucl. Chem.*, **41**, 1053 (1979); *Indian J. Chem.*, **17**, 296 (1979).
2. S.C. Tyagi and A.A. Khan, *J. Inorg. Nucl. Chem.*, **41**, 1899 (1979).
3. L. Baltgalve, G. Rudzitis, B. Petrov and N. Pucc., *Latv. Ps. R. Zinat Akad. Vestis, Kim. Ser.*, 582 (1988).
4. A. Jurenas, V.I. Pogonium and A.K. Chibisov, *Zh. Anal. Khim.*, **43**, 1657 (1988).
5. Abbasi, Abbas and Shahid, *Chem. Era*, **15**, 8 (1979).
6. A.A. Abdel-Gaber, M.B. Saleh and I.T. Ahmed, *J. Indian Chem. Soc.*, **69**, 17 (1992).
7. M.S. Abu-Bakr, K.A. Idriss, M.K. Hassan and H. Sedaira, *J. Indian Chem. Soc.*, **68**, 59 (1991).
8. C.R. Dhat and D.V. Jahagirdar, *Indian J. Chem.*, **21A**, 792 (1982).
9. R.K.P. Singh, P.C. Yadav and K.L. Yadava, *Natl. Acad. Sci. Lett.*, **4**, 437 (1981).
10. Y.Z. Yousif, A. Imarh and J.M. Faris, *J. Inorg. Nucl. Chem.*, **42**, 779 (1980).
11. P.K. Basu, *J. Indian Chem. Soc.*, **68**, 92 (1991).
12. K. Burger, Coordination Chemistry: Experimental Methods, Butterworth and Co. Ltd., London (1973).
13. K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, Wiley, New York (1963).
14. O.P. Pandey, S.K. Sengupta and S.C. Tripathi, *Synth. React. Inorg. Met.-Org. Chem.*, **13**, 867 (1983).
15. P.R.M. Shukla and A.K. Pathak, *J. Indian Chem. Soc.*, **67**, 678 (1990).
16. J. Basset, R.C. Denney, G.H. Jeffrey and J. Mendham, Vogel's Text Book of Quantitative Inorganic Analysis, Longman Group Ltd., London (1978).
17. R. Nayan and A.K. Dey, *Indian J. Chem.*, **14A**, 892 (1976).
18. G.F. Condike and A.E. Martell, *J. Inorg. Nucl. Chem.*, **31**, 2455 (1969).
19. P.R Rastogi, M. Singh and R. Nayan, *J. Indian Chem. Soc.*, **68**, 158 (1991).
20. D.D. Perrin, I.G. Sayce and V.S. Sharma, *J. Chem. Soc.*, 1755 (1967).
21. P.R. Rastogi, Ph.D. Thesis, Rohilkhand University, India (1989).

(*Received*: 30 March 1995; *Accepted:* 30 June 1995) AJC-995