

## Stability Constants of Some Uranyl Complexes

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Complexes of uranyl ion with benzoic, phenylacetic, phenoxy-acetic, thiomalic and itaconic acids were studied by pH titration method at  $31 \pm 0.1^\circ\text{C}$ . A 1 : 1 complex is formed in all the cases in the pH range 2.5—3.5 and their stability constants are reported.

In a potentiometric study of chelates of Uranyl nitrate with hydroxy, mercapto and amino acids, Cefola and coworkers<sup>1)</sup> reported the first and second formation constants of uranyl-thiomalate complex in the pH range 2—4, neglecting the hydrolysis of uranyl ion till pH 4.00. Later, Mathur, Nigam and Srivastava<sup>2)</sup> in a spectrophotometric study (Job's method) of the uranyl-thiomalic acid system reported the formation constants of the 1 : 1 complex in the pH range 3—7, neglecting again the hydrolysis of uranyl ions. It may be mentioned here that extensive investigations by Sutton,<sup>3)</sup> Ahrlund<sup>4)</sup> and recently by Sommer<sup>5)</sup> revealed that hydrolytic species of the type  $\text{U}_2\text{O}_5^{2+}$ ,  $\text{U}_3\text{O}_8^{2+}$ ,  $\text{U}_3\text{O}_8(\text{OH})$ ,  $(\text{UO}_2)_2(\text{OH})_2$ ,  $(\text{UO}_2)_2\text{OH}$ , etc., at  $\text{pH} > 3.5$  were present. As a part of our studies on complexes, systems of uranyl ion with benzoic, phenyl acetic, phenoxy acetic, thiomalic and itaconic acids were studied by pH titration method at  $31 \pm 0.1^\circ\text{C}$  with a view to determine the composition(s) and formation constant(s) of the complex(es) and to detect possible formation of polymeric species especially in the systems of uranyl ion with thiomalic and itaconic acids in the pH range 1.5—3.5 in which hydrolysis of uranyl ion may be completely neglected.

From the results of our studies, it is concluded that a 1 : 1 complex is formed in all the systems. The stability constants of all the complexes were evaluated at  $31 \pm 0.1^\circ\text{C}$ .

## Experimental

**Materials.** The uranyl perchlorate prepared from uranyl nitrate (BDH, AnalaR) by the standard procedure<sup>6)</sup> was assayed by the Jones reductor method<sup>7)</sup>

for uranyl content and by cation resin exchange method<sup>8)</sup> for free acid. A stock solution (0.26 M in uranyl and 0.09 M in hydrogen ion) was prepared. Carbonate free sodium hydroxide (1.0 M) was used in all the titrations, the former after dilution to ten times was standardized against potassium hydrogen phthalate (0.1 M). The ligand acids (A. R.; all correct M. ps) were standardized with sodium hydroxide solution (0.2 M). Deionised water free from carbonate was used in all the titrations. Sodium perchlorate (2.008 M) prepared from perchloric acid (60% G. R., E. Merck) and AnalaR sodium hydroxide was used for constancy of ionic strength at 0.1.

**Procedure.** A pH meter (Cat. No. 7666, Leeds and Northrup) with glass and calomel electrodes standardized with potassium hydrogen phthalate buffer (0.05 M; pH 4.01 at  $31^\circ\text{C}$ ) was used for measurements of pH during titrations of the system, ligand - perchloric acid - sodium perchlorate with or without uranyl perchlorate against standard alkali (1.0 M). All titrations were carried out in a double walled glass titration vessel provided with inlet and outlet tubes for circulating water at constant temperature ( $31^\circ\text{C}$  or  $45^\circ\text{C}$ ). The cell was covered with black cloth during titrations. Nitrogen freed from carbon dioxide was continually passed through the system under study in the titration cell. After each addition of the alkali titrant (0.05 ml), solutions were allowed to stand for 10—15 min for attainment of equilibrium. The titrations were carried out from an initial pH 1.5 to 11.0 and for ratios of [Ligand/Uranyl]  $\equiv$  1 to 10.

## Results and Discussion

**pH Titrations.** Acid dissociation constants of the ligand acids were determined by titrating systems of ligand - perchloric acid - sodium perchlorate against standard sodium hydroxide solution (1.0 M). The initial volume of the solution was 100 ml and the ionic strength was kept at 0.1. pHs of the solution were recorded after each addition of

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2) V. K. Mathur, H. L. Nigam and S. C. Srivastava, *This Bulletin*, **36**, 1658 (1963).

3) J. Sutton, *J. Chem. Soc.*, **1949**, (Suppl) 2, S-275.

4) A. Ahrlund, S. Hietanen and L. G. Sillen, *Acta Chem. Scand.*, **8**, 1907 (1954); S. Hietanen and L. G. Sillen, *ibid.*, **13**, 1828 (1959).

5) M. Bartusek and L. Sommer, *Z. Phys. Chem. (Leipzig)*, **226**, 309 (1964).

6) J. Heidt and A. Moon, *J. Am. Chem. Soc.*, **75**, 5803 (1953).

7) A. I. Vogel, "Text Book of Quantitative Inorganic Analysis," Longmans Green & Co., Ltd., (1962), p. 333.

8) D. W. Bhatnagar, *J. Sci. Ind. Res. (India)*, **B16**, 23 (1957).

0.05 ml of sodium hydroxide solution. Acid dissociation constants of benzoic, phenyl acetic and phenoxy acetic acids were calculated by the algebraic method and those of thiomalic and itaconic acids (first,  $K_1$  and second,  $K_2$ ) were determined conveniently by the method of slope and intercept due to Irving and Rossotti<sup>9)</sup> because the two inflexions in the titration curves overlapped to give single inflexion points in the latter two cases. The following equation<sup>9)</sup> due to Irving and Rossotti was used:

$$\frac{\bar{n}_H}{(1-\bar{n}_H)[H]} = \frac{1}{K_2} + \frac{1}{K_1 K_2} \frac{(2-\bar{n}_H)[H]}{(1-\bar{n}_H)} \quad (1)$$

$$K_1 = [HA][H]/[H_2A] \text{ and } K_2 = [H][A]/[HA]$$

$\bar{n}_H$ , the average number of hydrogen ions bound to a ligand anion and corresponds to the Bjerrum's formation function<sup>10)</sup>; charged species  $H^+$  are written as  $H$  for simplicity. The  $pK_1$  and  $pK_2$  values for all acids are given in Table 1. A value of 0.83 for activity coefficient for  $H^+$  (0.1 N) was used<sup>11)</sup> for computing the concentration of the latter.  $pK$  values for various acids with those reported in literature<sup>12-14)</sup> are given (Table 1).

TABLE 1.  
Temperature 31°C  $\mu=0.1$  (NaClO<sub>4</sub>)

Ligand	$pK(\text{Authors})$		$pK(\text{Lit.})$		$\log K_{ML}^*$
	$pK_1$	$pK_2$	$pK_1$	$pK_2$	
1. Benzoic acid	4.01	—	4.01 <sup>14a)</sup>	—	2.59
2. Phenyl acetic acid	4.20	—	4.557 <sup>14b)</sup>	—	3.25
3. Phenoxy acetic acid	2.96	—	2.93 <sup>12)</sup>	—	2.41
4. Thiomalic acid	3.01	4.51	3.22	4.69 <sup>13)</sup>	3.75
5. Itaconic acid	3.61	5.08	3.68	5.14 <sup>14a)</sup>	4.85**

\* Concentration constants

\*\* Temperature: 28°C

**Stability Constants  $K_{ML}$ .** A known concentration,  $C_L$ , of the ligand was titrated without and with a known concentration,  $C_M$ , or uranyl ion, so that  $[C_L/C_M]=1$  or 2 to facilitate formation of com-

plexes 1 : 1 ( $ML_1$ ) and 1 : 2 ( $ML_2$ ) respectively. Titrations were also carried out for  $[C_L/C_M]=10$  to allow the formation of higher complexes, if any. The degrees of formation of the metal complexes,  $\bar{n}$ , were calculated from the titration curves by Irving and Rossotti's difference method.<sup>15)</sup> Values for the log of free ligand concentration,  $pL$  were obtained from the equation:

$$pL = \log_{10} \frac{\{1 + ([H]/K_2) + ([H]^2/K_1 K_2)\}}{(C_L - \bar{n}C_M)} \quad (2)$$

Values of  $\bar{n}$  and  $pL$  were used to draw the formation curves for the systems and  $\log K_{ML}$  of the complex was evaluated from the value of  $pL$  at  $\bar{n}=0.5$  (Fig. 1a). The stability constants were also determined graphically using Eq. (3), also due to Irving and Rossotti.<sup>9)</sup>

$$\frac{\bar{n}}{(1-\bar{n})[L]} = K_{ML} + K_{ML} K_{ML_2} \frac{(2-\bar{n})[L]}{(1-\bar{n})} + \sum_{n=3}^N K_{ML} K_{ML_2} \cdots K_{ML_n} \frac{(n-\bar{n})[L]^{n-1}}{(1-\bar{n})} \quad (3)$$

$K_{ML}$ ,  $K_{ML_1}$ , ...,  $K_{ML_n}$  = successive formation constants and  $[L]$  = free ligand concentration. The formation of only 1 : 1 complex was also obvious from the plots  $\bar{n}/(1-\bar{n})[L]$  vs.  $(2-\bar{n})[L]/(1-\bar{n})$  being parallel to the abscissa (Fig. 1b). The stability constants calculated from  $\bar{n}$  vs.  $pL$  curve agreed very well with those calculated from Eq. (3). It may be mentioned that  $\bar{n}$  did not go beyond unity even when  $[C_L/C_M] \geq 1$  up to 10. From the order of stability constants (Table 1) for phenoxy acetic acid and benzoic acid being similar it appears that a chelate ring involving phenoxy oxygen atom is not formed for  $UO_2^{2+}$ -phenoxy acetic acid complex. The difference in the stability constant values between phenyl acetic acid and phenoxy acetic acids may be due to the respective  $pK$  values being different and therefore affecting considerably the stabilities of the complexes formed.<sup>16,17)</sup> No data for stability constants for  $UO_2^{2+}$ -monobasic acid complexes (studied by us) are available in literature for comparison.

**Thiomalic and Itaconic Acids.** The formation curves of these systems showed the formation of only 1 : 1 complex in the pH range (1.5—3.5) (Fig. 1a and 1b). In order to detect the possible polymerization of the  $UO_2^{2+}$ -thiomalate and  $UO_2^{2+}$ -itaconate complexes, the pH titrations of the 1 : 1 uranyl-thiomalate and uranyl-itaconate systems were carried out for  $[UO_2^{2+}] = [Ligand] = 0.02$  M, 0.008 M, 0.005 M, 0.0025 M and 0.001 M for the former and 0.02 M, 0.0032 M, and 0.0016 M for the latter system which amounts to variation in

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17) H. Irving and H. Rossotti, *Acta Chem. Scand.*, **10**, 72 (1956).

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10) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," Hasse, Copenhagen (1941).

11) J. Kielland, *J. Am. Chem. Soc.*, **59**, 1675 (1937).

12) K. Suzuki and K. Yamasaki, *J. Inorg. Nucl. Chem.*, **24**, 1093 (1962).

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14) a) M. Yasuda, K. Yamasaki and H. Okutaki, *This Bulletin*, **33**, 1067 (1960). b) "Stability Constants," 2nd Ed., ed. by L. G. Sillen and A. E. Martell, The Chemical Society, London (1964), p. 567.

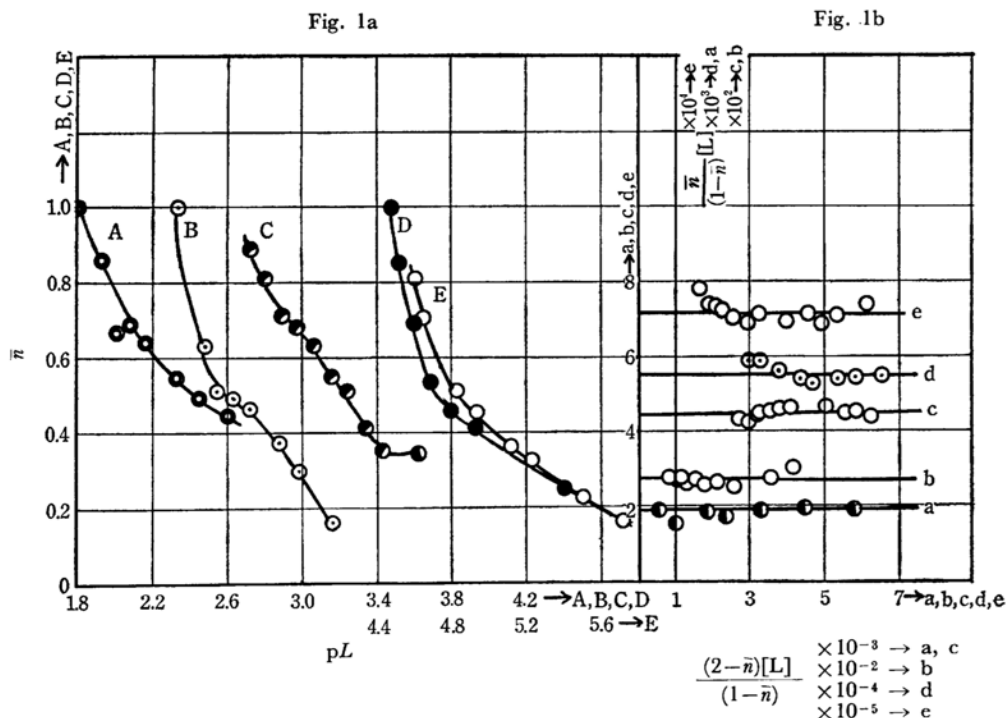


Fig. 1a. Formation curves ( $\bar{n}$  vs.  $pL$ ) of the systems of  $UO_2^{2+}$  with (A) Phenoxy acetic acid, (B) Benzoic acid, (C) Phenyl acetic acid, (D) Thiomalic acid, (E) Itaconic acid.

Fig. 1b. Plots of  $\frac{\bar{n}}{(1-\bar{n})} \frac{[L]}{[L]}$  vs.  $\frac{(2-\bar{n})[L]}{(1-\bar{n})}$  of  $UO_2^{2+}$  with (a) Phenyl acetic acid, (b) Phenoxy acetic acid, (c) Benzoic acid, (d) Thiomalic acid, (e) Itaconic.

TABLE 2

Ionic strength = 0.1 ( $NaClO_4$ )

Acid dissociation constants

Thiomalic acid  $pK_1 = 3.01$ ;  $pK_2 = 4.51$  ( $31^\circ C$ )

$pK_1 = 2.95$ ;  $pK_2 = 4.45$  ( $45^\circ C$ )

Itaconic acid  $pK_1 = 3.61$ ;  $pK_2 = 5.08$  ( $28^\circ C$ )

$T_M =$ $T_L(M) \times 10^3$	$\log K_{ML}$ $31^\circ C$	$\log K_{ML}$ (av.). $31^\circ C$	$\log K_{ML}$ (av.). $45^\circ C$
UO <sub>2</sub> <sup>2+</sup> -Thiomalate			
20	3.75	3.82±0.08	3.91±0.08
8	3.89		
5	4.01		
2.5	4.00		
UO <sub>2</sub> <sup>2+</sup> -Itaconate			
20	4.85	4.72±0.13	
3.2	4.58		
1.6	4.73		

the total ligand and total metal concentrations by factors of 20 and 12 respectively. The data (Table 2) show that the  $\log K_{ML}$  values for the uranyl-thiomalate and uranyl-itaconate systems increase slightly with decreasing concentration of the metal chelates and therefore polymeric complexes may be assumed to be absent in these systems.<sup>18)</sup> We

restricted our studies to  $pH < 3.5$  so that hydrolytic equilibria did not interfere with the systems under consideration.

pH titrations of the thiomalic acid against sodium hydroxide with and without uranyl ion were also carried out by us at  $45^\circ C$ . The stability constants for uranyl-thiomalic acid system at  $31^\circ C$  and  $45^\circ C$  (Table 2) did not vary very much within the limits of experimental errors and therefore calculation of thermodynamic parameters  $\Delta H$  and  $\Delta S$  under these circumstances would be futile according to Rossotti<sup>19)</sup> and therefore no attempts for calculation of these parameters were made by us. Values of stability constants for uranyl-itaconic acid complex are not available in literature for comparison. Our value for the stability constant for  $UO_2^{2+}$ -thiomalic acid complex has been calculated under conditions of negligible hydrolysis and least complexing medium and therefore represents an improvement over the values already reported.<sup>1,2)</sup>

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19) F. J. C. Rossotti, "Modern Coordination Chemistry, Principles and Methods," Interscience Publishers, New York (1960), p. 18.

### Conclusion

From our results, it is evident that uranyl ion forms a 1 : 1 complex with all the ligands under study in the pH range, (1.5—3.5). This is the case even when the ratio [Ligand/Uranyl]=1 to 10.

It is probable that itaconic acid may coordinate through two  $\text{COO}^-$  groups to uranyl ion, forming a chelate ring. But in the case of thiomalic acid, a consideration of magnetic susceptibility data of uranyl-thiomalate complex by Mathur *et al.*,<sup>20</sup> and comparison of the  $\log K_{ML}$  (3.75) for the latter with that for uranyl-malate complex ( $\log K_{ML}=1.66$ )<sup>18</sup>) under more or less identical conditions indicate the possible involvement of neutral sulfur

atom in coordination to uranyl forming a chelate ring, similar to coordination of neutral oxygen in hydroxy acids to metal ions.<sup>20,21</sup>) The possibility of coordination of  $\text{S}^-$  to  $\text{UO}_2^{2+}$  cannot be discounted. The coordination of  $-\text{SH}$  group to metal ion even in the acidic region resulting in the deprotonation of the former is possible; however, we were unable to detect the release of the third proton in the pH range 2.0 to 5.0 of our studies. (Absence of inflexion corresponding to the release of third proton in our plots of pH *vs.* "moles of base"/"mole of ligand" added.)

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