

pH-metric Studies on Binary, Ternary and Quaternary Complexes of Dioxouranium(VI)

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Manuscript received 20 October 1978, accepted 21 June 1979

The detailed potentiometric investigations have been carried out on the system UO_2 -oxalic acid-malonic acid-aminodiacetic acid. The formation constants and free energies of formation for all the possible binary, ternary and quaternary complexes formed, have been evaluated. 1 : 1 : 1 : 1 quaternary complexes have been found to be more stable than 1 : 1 : 1 ternary or 1 : 1 binary complexes.

THE binary complexes¹⁻¹⁰ of dioxouranium with different carboxylic, hydroxy and aminopolycarboxylic acids have been extensively studied, but much less work has been undertaken on the heteroligand ternary¹¹⁻¹⁷ and quaternary¹⁸ systems involving dioxouranium ion. In continuation of the earlier communication¹⁹ on the potentiometric studies of the quaternary systems involving uranyl ion and a number of dibasic acids, the authors report the detailed investigations on UO_2 -OX-Maln-IMDA systems (where OX=oxalic acid, Maln=malonic acid and IMDA=aminodiacetic acid) in the present communication.

Experimental

All the chemicals used were of BDH AnalaR grade. The stock solution of $UO_2(NO_3)_2$ was prepared and the metal was estimated gravimetrically as U_3O_8 . The ligand solutions were prepared by direct weighing and the concentrations of the solutions were further checked by potentiometric titration against 0.1 M KOH. The concentration of the solutions (5×10^{-3} M in metal or ligand), total volume (50 ml) and ionic strength ($\mu=0.1$ M KNO_3) were always kept constant at the beginning of the titration.

pH measurements were made with Philips precision pH-meter (PR 9405 M) (accuracy ± 0.02) using standard glass (PV 9011) and calomel (PV 9021) electrodes. The instrument was standardised against 0.05 M potassium hydrogen phthalate for pH-4 at temperature $25 \pm 1^\circ$ before use.

The dissociation constants (Table 1) were determined by the method of Chaberek and Martell²⁰ or

TABLE 1

Ligand	pK_1	pK_2
Oxalic acid	1.66	3.90
Malonic acid	2.75	5.36
Iminodiacetic acid	2.54	9.18

TABLE 2

System	Stoichiometry	$\log K$	ΔF° (K cal/mole)
UO_2 -OX	1 : 1	$9.97 \pm .27$	- 5.41
	1 : 2	$9.08 \pm .25$	-12.37
	1 : 3	$16.40 \pm .12$	-22.35
UO_2 -Maln	1 : 1	$5.56 \pm .18$	- 7.57
	1 : 2	$12.18 \pm .18$	-16.60
UO_2 -IMDA	1 : 1	$8.83 \pm .15$	-12.03
UO_2 -OX-Maln	1 : 1 : 1	$7.67 \pm .11$	-10.45
	1 : 2 : 1	$14.32 \pm .24$	-19.51
UO_2 -OX-IMDA	1 : 1 : 1	$10.07 \pm .28$	-13.72
	1 : 2 : 1	$13.65 \pm .11$	-18.60
UO_2 -Maln-IMDA	1 : 1 : 1	$11.44 \pm .09$	-15.59
	1 : 2 : 1	$18.19 \pm .11$	-24.79
UO_2 -OX-Maln-IMDA	1 : 1 : 1 : 1	$11.55 \pm .15$	-15.74

Noyes²¹ and the formation constants (Table 2) for the binary, ternary and quaternary species by the expressions given in Table 3. Free energies of formation were calculated from the following expression. $\Delta F^\circ = -RT \ln K$

Hydrolysis and polymerisation of the complexes were supposed to be negligible in the pH range (2-3) where calculations were made.

Results and Discussion

The curve representing the pH-metric titration of $UO_2(NO_3)_2$ with KOH is similar to that obtained by Feldman et al.^{22,23}, a sharp inflection observed at $m \sim 2.3$ (m =moles of alkali added per mole of metal or ligand) being attributed to the species such as $U_2O_8^{2+}$, $U_3O_8^{2+}$, $U_3O_8(OH)^+$, $U_3O_8(OH)_2$, etc.

Inflections at $m=2$ in the curves a and a' for OX and Maln respectively and at $m=1$ in curve a'' for IMDA may be correlated to the titration of both the carboxylic protons in case of oxalic and malonic acid while only one of the carboxylic protons is titrated in the case of IMDA.

Binary Systems :

Curves b, b' and b'' (Fig. 1) representing the titration of 1 : 1 UO_2 -OX/Maln/IMDA systems

TABLE 3

System	Formation Constant	A	X
1 : 1	$K_{ML} = \frac{T_M - A \cdot X}{A^2 \cdot X}$	$\frac{M - T_{OH} - H^+}{\frac{2H^{+2}}{K_1 K_2} + \frac{H^+}{K_2}}$	$1 + \frac{H^{+2}}{K_1 K_2} + \frac{H^+}{K_2}$
1 : 2	$K_{ML_2} = \frac{T_M - 1/2A \cdot X}{(\frac{1}{2})^2 A^2 \cdot X}$	$\frac{4T_M - T_{OH} - H^+}{\frac{2H^{+2}}{K_1 K_2} + \frac{H^+}{K_2}}$	$1 + \frac{H^{+2}}{K_1 K_2} + \frac{H^+}{K_2}$
1 : 3	$K_{ML_3} = \frac{T_M - \frac{1}{3}A \cdot X}{(\frac{1}{3})^3 A^3 \cdot X}$	$\frac{6T_M - T_{OH} - H^+}{\frac{2H^{+2}}{K_1 K_2} + \frac{H^+}{K_2}}$	$1 + \frac{H^{+2}}{K_1 K_2} + \frac{H^+}{K_2}$
1 : 1 : 1	$K_{MLL'} = \frac{T_M - \frac{1}{3}A \cdot X}{(\frac{1}{3})^3 A^3 \cdot X}$	$\frac{4T_M - T_{OH} - H^+}{\frac{4H^{+2}}{K_1 K_2 + K_1' K_2'} + \frac{2H^+}{K_2 + K_2'}}$	$1 + \frac{2H^{+2}}{K_1 K_2 + K_1' K_2'} + \frac{2H^+}{K_2 + K_2'}$
1 : 2 : 1	$K_{ML_2 L'} = \frac{T_M - \frac{1}{3}A \cdot X}{(\frac{1}{3})^3 A^3 \cdot X}$	$\frac{6T_M - T_{OH} - H^+}{\frac{6H^{+2}}{2K_1 K_2 + K_1' K_2'} + \frac{3H^+}{2K_2 + K_2'}}$	$1 + \frac{3H^{+2}}{2K_1 K_2 + K_1' K_2'} + \frac{3H^+}{2K_2 + K_2'}$
1 : 1 : 1 : 1	$K_{MLL' L''} = \frac{T_M - \frac{1}{3}A \cdot X}{(\frac{1}{3})^3 A^3 \cdot X}$	$\frac{6T_M - T_{OH} - H^+}{\frac{6H^{+2}}{K_1 K_2 + K_1' K_2' + K_1'' K_2''} + \frac{3H^+}{K_2 + K_2' + K_2''}}$	$1 + \frac{3H^{+2}}{K_1 K_2 + K_1' K_2' + K_1'' K_2''} + \frac{3H^+}{K_2 + K_2' + K_2''}$

$T_M = [\text{Metal}]_{\text{total}}$, $T_{OH} = \text{KOH}$, K_1, K_2, K_1', K_2' and K_1'', K_2'' and K_2'' are the acid dissociation constants of the ligands.

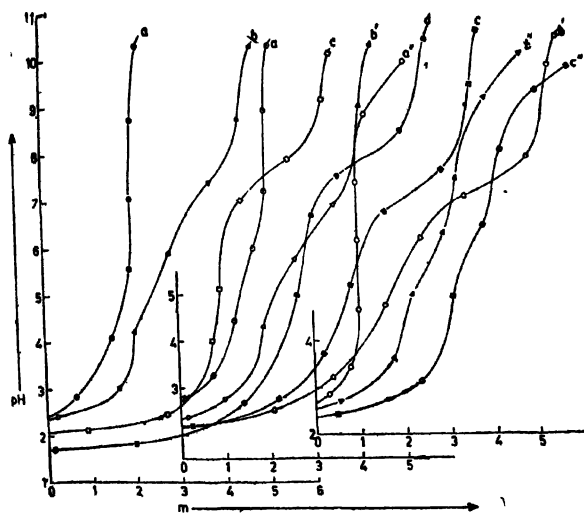


Fig. 1. Curve a=OX, b=1 : 1 UO_2 -OX, c=1 : 2 UO_2 -OX, d=1 : 3 UO_2 -OX, a'=Maln, b'=1 : 1 UO_2 -Maln, c'=1 : 2 UO_2 -Maln, d'=1 : 3 UO_2 -Maln, a''=IMDA, b''=1 : 1 UO_2 -IMDA, c''=1 : 2 UO_2 -IMDA

exhibit inflections at $m=2$, which may be attributed to the formation of 1 : 1 binary complexes undergoing hydrolysis and polymerisation in the higher pH range.

Curves c, c' and c'' represent the titration of 1 : 2 UO_2 -OX/Maln/IMDA systems. The lowering in pH

exhibited by the curves c and c' in comparison to those indicating respective 1 : 1 systems, an inflection at $m=4$ and the non-superimposable nature of the theoretical composite curve (drawn by adding the horizontal distances of the curves for 1 : 1 UO_2 -OX/Maln and free ligand), indicate the formation of 1 : 2 complex of uranyl ion with dicarboxylic acid. An inflection at $m=3$ in the case of 1 : 2 UO_2 -IMDA system may, however, be attributed to the formation of a 1 : 1 UO_2 -IMDA complex and the simultaneous titration of remaining IMDA.

Curves for the titration of 1 : 3 UO_2 -OX/Maln/IMDA systems give an evidence for the formation of 1 : 3 complex in the case of oxalic acid only.

Ternary Systems :

Curves e, f, g represent the titration of 1 : 1 : 1 UO_2 -OX-Maln, UO_2 -OX-IMDA and UO_2 -Maln-IMDA systems respectively. The lowering in pH in comparison to 1 : 1 binary systems and an inflection at $m=4$ may be correlated to the simultaneous addition of the two ligands to the central Oxo metal ion forming heteroligand ternary complex. 1 : 2 : 1 UO_2 -OX-Maln, UO_2 -OX-IMDA and UO_2 -Maln-IMDA systems were also investigated and the formation constants for the resulting 1 : 2 : 1 ternary species were evaluated.

Quaternary Systems :

Curve h represents the titration of uranyl ion in presence of isomolar quantities of oxalic, malonic

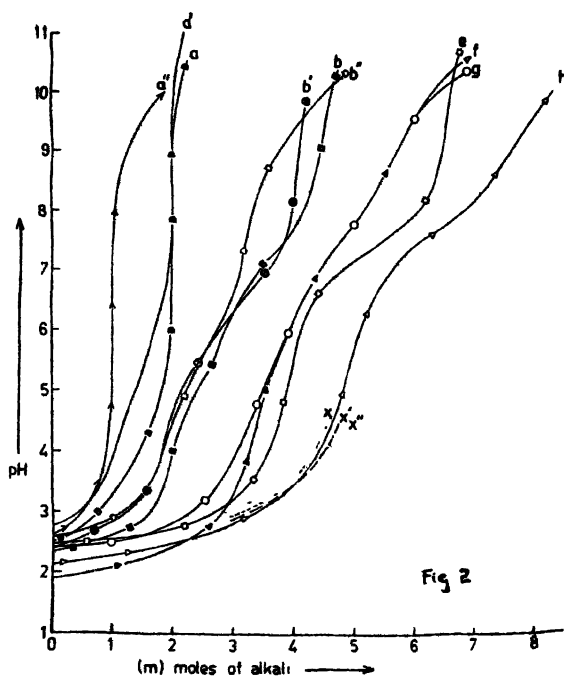


Fig. 2. Curve a=OX, a'=Maln, a''=IMDA, b=1:1 UO₂-OX, b'=1:1 UO₂-Maln, b''=1:1 UO₂-IMDA, e=1:1:1 UO₂-OX-Maln, f=1:1:1 UO₂-OX-IMDA, g=1:1:1 UO₂-Maln-IMDA, h=1:1:1:1 UO₂-OX-Maln-IMDA, x, x' and x'' are theoretical composite curves.

acid and IMDA. The formation of a quaternary complex is evidenced by the lowering in pH, difference in precipitation pH and by the non-superimposable nature of the theoretical composite curves x, x' and x'' (drawn by adding the horizontal distances of the curves for (i) UO₂-OX-Maln and IMDA, (ii) UO₂-OX-IMDA and Maln and (iii) UO₂-Maln-IMDA and oxalic acid) in the region of quaternary complex formation.

The comparison of the stability constants indicate that 1:1:1:1 quaternary complexes are more stable than 1:1:1 ternary or 1:1 binary complexes. In case of binary systems IMDA forms the most stable complex with uranyl ion and in case of ternary systems the most stable complexes are formed in the systems involving malonic acid and IMDA. The observed trend in the value of the formation constants may be ascribed to the increasing basicities of the ligands.

Acknowledgement

Authors thank Dr. J. P. Tandon, Prof. and Head Chemistry Department, Rajasthan University, Jaipur for his valuable suggestions. They also thank Dr. S. M. L. Gupta for laboratory facilities and CSIR for the award of PDF to one of them (V. K.).

References

1. KUAN PAN, Tong. Ming, Hsueh and Teh-Liang Chaing, *J. Chinese Chem. Soc.*, Ser II, 1957, 4.
2. C. V. BANKS and R. S. SINGH, *J. Inorg. Nuclear Chem.*, 1960, 15, 125.
3. R. T. OLIVER and J. S. FRITZ., U. S. Atomic Energy Commission ISC, 1958, 41, 1056.
4. S. O. TRIPATHI, *J. Indian Chem. Soc.*, 1958, 35, 119.
5. V. T. ATHAVALE, N. MAHADEVAN and R. N. SATHI, *Indian J. Chem.*, 1968, 6, 660.
6. S. RAMAMOORTHY and M. SANTAPPA, *Bull. Chem. Soc., Japan*, 1969, 42, 411.
7. P. N. PALER, Peaceful uses of Atomic Energy Proceeding of the International Conference, Geneva, 1955, 8.
8. A. K. MUKHERJEE and A. K. DEY, *J. Indian Chem. Soc.*, 1968, 35, 113.
9. S. RAMAMOORTHY and M. SANTAPPA, *Bull. Chem. Soc., Japan*, 1968, 41, 1330.
10. S. K. VERMA and R. P. AGARWAL, *J. of Less Common Metals*, 1967, 12, 221.
11. S. RAMAMOORTHY and M. SANTAPPA, *J. Inorg. Nuclear Chem.*, 1970, 32, 1623.
12. G. H. CARRY and A. E. MARTELL, *J. Amer. Chem. Soc.*, 1967, 89, 2859.
13. M. S. BALKRISHNAN and M. SANTAPPA, *J. Inorg. Nuclear Chem.*, 1975, 37, 1929.
14. S. H. EBERLA and W. REBEL, *Inorg. Nuclear Chem., Lett.*, 1968, 4, 113.
15. V. P. KHANOLKAR, D. V. JAHAGIRDAR and D. P. KHANOLKAR, *J. Inorg. Nuclear Chem.*, 1973, 35, 931.
16. P. V. SELVARAJ and M. SANTAPPA, *Curr. Sci.*, 1972, 41, 872.
17. M. S. BALKRISHNAN and M. SANTAPPA, *J. Inorg. Nuclear Chem.*, 1974, 36, 3813.
18. S. RAMAMOORTHY and M. SANTAPPA, *J. Inorg. Nuclear Chem.*, 1971, 33, 1775.
19. VINOD KUMARI and G. K. CHATURVEDI, *J. Indian Chem. Soc.*, 1978, 55, 319.
20. S. CHABEREK and A. E. MARTELL, *J. Amer. Chem. Soc.*, 1952, 74, 5052.
21. ARTHUR A. NOYES, *J. Physik. Chem.*, 1893, 11, 498.
22. I. FELDMAN, J. R. HAVILL and W. F. NEWMAN, *J. Amer. Chem. Soc.*, 1954, 73, 4726.
23. W. F. NEWMAN, J. R. HAVILL and I. FELDMAN, *J. Amer. Chem. Soc.*, 1957, 76, 3592.