STABILITY CONSTANTS OF MIXED-LIGAND COMPLEXES OF URANYL ION WITH CARBOXYLIC ACIDS

EARLIER studies[1] on the simple complexes of uranyl ion with various carboxylic acids revealed that 1 : 1 complexes were usually formed except with pyruvic acid where a weak 1 : 2 complex was formed. The present investigation deals with studies on mixed complexes[2-4] involving UO_2^{++} and systems of (i) monobasic acid + monobsaic acid, (ii) monobasic acid + dibasic acid and (iii) dibasic acid + dibasic acid.

The preparation of uranyl perchlorate as well as other reagents and their estimations have been given earlier[1]. The details of

apparatus and the experimental technique used to obtain the Bjerrum-Calvin titration curves, methods of calculations of dissociation constants of ligand acids by Irving and Rossotti's method[5,6] were substantially the same as outlined earlier by Ramamurthi and Santappa[1]. The equations employed to evaluate the stability constants of the UO_2^{++}-mixed-ligand complexes were outlined earlier by Ramamurthi and Santappa[2,3,7] and the calculations of stability constants were done using IBM 1130 computer.

Analysis of the Bjerrum-Calvin pH titration curves of these systems, indicated the formation of mixed-ligand complexes as evident from (a) the shift of the precipitation points of the mixed-ligand complexes from that of the corresponding simple complexes, (b) the non-superimposibility of titration curves on one another, (c) a fair constancy in the log K_{MLL}', values over a wide range of pH values for all the systems. We report the stability constants with error limits for various mixed-ligand complexes in Table I.

TABLE I

Stability constants of mixed-ligand complexes of UO_2^{++}. UO_2^{++} as $UO_2(ClO_4)_2$

$\mu = 0.1 M\ (NaClO_4)$; $\qquad T = 31 \pm 0.1\ ^\circ C$

No.	Ligand$_1$	Ligand$_2$	Stability constant Log K_{MLL}'
I	Monobasic acid-Monobasic acid:		
1	Phenoxy acetic acid	Pyruvic acid	$5 \cdot 62 \pm 0 \cdot 04$
II	Monobasic acid-Dibasic acid:		
2	Phenoxy acetic acid	Fumaric acid	$6 \cdot 20 \pm 0 \cdot 01$
3	,,	Maleic acid	$8 \cdot 75 \pm 0 \cdot 02$
4	,,	Thiomalic acid	$8 \cdot 62 \pm 0 \cdot 05$
5	,,	Itaconic acid	$9 \cdot 29 \pm 0 \cdot 01$
6	,,	Succinic acid	$8 \cdot 66 \pm 0 \cdot 08^*$
7	,,	Adipic acid	$8 \cdot 78 \pm 0 \cdot 09$
8	Pyruvic acid	Fumaric acid	$7 \cdot 43 \pm 0 \cdot 01$
9	,,	Maleic acid	$10 \cdot 55 \pm 0 \cdot 03$
10	,,	Thiomalic acid	$9 \cdot 07 \pm 0 \cdot 01$
11	,,	Itaconic acid	$10 \cdot 11 \pm 0 \cdot 03$
12	,,	Succinic acid	$10 \cdot 05 \pm 0 \cdot 01$
13	,,	Adipic acid	$10 \cdot 52 \pm 0 \cdot 02$
III	Dibasic acid-Dibasic acid:		
14	Fumaric acid	Maleic acid	$7 \cdot 06 \pm 0 \cdot 01$
15	,,	Thiomalic acid	$7 \cdot 13$
16	,,	Itaconic acid	$6 \cdot 42 \pm 0 \cdot 01$
17	,,	Succinic acid	$5 \cdot 98 \pm 0 \cdot 03$
18	,,	Adipic acid	$6 \cdot 21 \pm 0 \cdot 03$
19	Maleic acid	Thiomalic acid	$7 \cdot 37$
20	,,	Itaconic acid	$8 \cdot 16 \pm 0 \cdot 02$
21	,,	Succinic acid	$7 \cdot 53 \pm 0 \cdot 01$
22	,,	Adipic acid	$8 \cdot 09 \pm 0 \cdot 01$

* Value taken from Ref. 4.

From the results we conclude that:

(i) In the case of UO_2^{++}-phenoxy acetic acid-pyruvic acid system, which is a UO_2^{++}-monobasic acid-monobasic acid system, the stability constant is 5·62 which is of the same order of magnitude as other such systems studied earlier[4].

(ii) The UO_2^{++}-monobasic acid-dibasic acid systems: Phenoxy acetic acid and pyruvic acid are examples of the former and fumaric, maleic, thiomalic, itaconic, succinic and adipic acids are examples of the latter. Generally, the precipitation points of the systems UO_2^{++}-pyruvic acid-ligand$_2$ (any dicarboxylic acid) shifted to a higher pH $\cong$ 12, probably due to stabilization of the complex by the keto oxygen in pyruvic acid. The stability constants for these mixed complexes are of the order (ligand$_2$): maleic acid > adipic acid > itaconic acid > succinic acid > thiomalic acid > fumaric acid. The stabilities of UO_2^{++}-phenoxy acetic acid-ligand$_2$ (dicarboxylic acids) are of the order: itaconic acid > adipic acid > maleic acid > succinic acid > thiomalic acid > fumaric acid. UO_2^{++}-phenoxy acetic acid-fumaric acid has a stability constant comparable with that of the UO_2^{++}-monobasic acid-monobasic acid system[4]. The UO_2^{++}-pyruvic acid-dicarboxylic acids complexes have higher stability values over the UO_2^{++}-phenoxy acetic acid-dicarboxylic acids complexes.

(iii) In the case of UO_2^{++}-dibasic acid-dibasic acid, the systems studied were (i) fumaric acid and maleic acid with thiomalic, itaconic, succinic and adipic acids and (ii) fumaric acid with maleic acid. The UO_2^{++}-fumaric acid-ligand$_2$ (maleic, thiomalic, itaconic, succinic and adipic acids) complexes have been found to have lower stability values when compared with UO_2^{++}-maleic acid-ligand$_2$ (all dicarboxylic acids except fumaric acid) complexes. The stabilities of the UO_2^{++}-fumaric acid-ligand$_2$ complexes are of the order: thiomalic acid > maleic acid > itaconic acid > adipic acid > succinic acid. The stabilities of UO_2^{++}-maleic acid-ligand$_2$ complexes are of the order: itaconic acid > adipic acid > succinic acid > thiomalic acid.

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