COMPLEXES OF URANYL ION WITH VARIOUS CARBOXYLIC ACIDS

As a part of our studies on complexes of uranyl ion with organic acids, systems of uranyl ion with various acids (*see* Table I) were studied by pH titration method at 31° C. and $\mu = 0{\cdot}1$ ($NaClO_4$) with a view to determine the composition (s) and formation constant (s) of the complex (es) in the pH range 1·5–3·5 in which the hydrolysis of uranyl ion may be completely neglected.

A Leeds and Northrup pH meter (cat. no. 7666) with glass and calomel electrodes and standardized against 0·05 M potassium hydrogen phthalate solution (pH 4·01 at 31° C.) was used in the pH titrations. Uranyl perchlorate prepared by standard procedure[1] and estimated by Jone's reductor for uranyl content[2] and cation resin exchange for free acid content[3] was used as a source of uranyl ion. Carbonate-free sodium hydroxide was used as the titrant. All ligand acids were of analytical grade.

Dissociation constants of ligand acids and stability constants of various complexes were evaluated graphically as well as by least squares from the values of $\bar{n}_{H}$ and $\bar{n}$ by Irving and Rossotti's method.[4] The results are tabulated in Table I, along with those succinic and maleic acids were obtained under somewhat different experimental conditions of ionic strength (1 M KNO_3) and temperature (25° C.), (log K_{ML_1} and log K_{ML_2} for UO_2^{++}-malonic acid, 5·66, 4·00 and log K_{ML_1} for UO_2^{++}—succinic, UO_2^{++}— maleic acids are 3·68 and 4·46 respectively).

From our results, we may conclude that:

(*i*) in UO_2^{++}— simple monocarboxylic acids (formic, propionic, benzoic and phenyl acetic acids) systems, the pK of the ligand acid is of the order formic < benzoic < phenyl acetic < propionic while K_{ML_1} is formic = benzoic < phenyl acetic > propionic acid.

(*ii*) in UO_2^{++}— monocarboxylic acids containing —O— and $-\overset{\overset{\displaystyle O}{\|}}{C}-$ groups (phenoxy acetic and pyruvic acids), UO_2^{++}— phenoxy acetic acid system differed very much from UO_2^{++}— pyruvic acid in number of complexes formed as well as the stability range of the latter. Though the stability range of these systems showed the non-involvement of oxygen atom in co-ordination, probable stabilization by keto oxygen in UO_2^{++}— pyruvic acid was inferred from the facts that precipitation did not occur till pH 10·5 and complexation was considerable at low pH.

TABLE I

Dissociation constants of ligand acids and metal-ligand stability constants

Metal = UO_2^{++} $\mu = 0{\cdot}1$ ($NaClO_4$). T = 30 ± 0·1° C.

Ligand		Author's values		Literature		Author's values	
		$_pK_1$	$_pK_2$	$_pK_1$	$_pK_2$	log K_{ML_1}	log K_{ML_2}
1. Formic acid	..	3·54	..	..	..	2·61	..
2. Benzoic acid	..	4·01	..	4·01[7]	..	2·57	..
3. Phenyl acetic acid	..	4·12	..	..	..	3·21	..
4. Propionic acid	..	4·62	..	..	..	3·03	..
5. Phenoxy acetic acid	..	2·96	..	..	..	2·59	..
6. Pyruvic acid	..	2·39	..	..	..	2·15	0·59
7. Malonic acid	..	2·81	5·14	..	..	5·28	4·01
8. Succinic acid	..	3·87	5·12	..	..	4·48	..
9. Adipic acid	..	4·12	5·04	4·28	5·00[7]	4·08	..
10. Itaconic acid	..	3·61	4·98	3·68	5·14[7]	4·86	..
11. Thiomalic acid	..	2·95	4·45	..	..	3·71	..
12. Maleic acid	..	1·95	6·16	..	..	5·15	..
13. Fumaric acid	..	2·89	4·11	..	..	3·05	..
14. Diglycolic acid	..	2·77	3·88	2·77	3·92[7]	4·90	2·84
15. Crotonic acid	..	4·53	..	..	..	2·74	2·53

literature values obtained under comparable experimental conditions of ionic strength and temperature. It may be mentioned that we are reporting thirteen equilibrium constants for the first time, though reported data[5] on the stability constants in the case of malonic,

(*iii*) in UO_2^{++}— simple dicarboxylic acids (malonic, succinic and adipic acids), stability of the chelate ring decreases with increase in ring size, *i.e.*, from malonic → adipic acid and formation of 1 : 2 complex (UO_2^{++}— malonic acid) may be due to least steric hindrance.

(*iv*) in UO_2^{++}— substituted dicarboxylic acids (thiomalic and itaconic acids[6]), the chelate ring is stabilized by the presence of a double bond or by a —SH group and more so by the former.

(*v*) in UO_2^{++} — *cis* and *trans* dicarboxylic acids (maleic and fumaric acids), maleic acid formed a seven-membered chelate ring with UO_2^{++} while fumaric acid, being a *trans* isomer formed only a complex (not a chelate).

(*vi*) in UO_2^{++}— dicarboxylic acid containing —O— (diglycolic acid), diglycolic acid forms a chelate with UO_2^{++} with additional stabilization through —O— group as evident from K_{ML} value.

(*vii*) in UO_2^{++}— unsaturated carboxylic acid (crotonic acid), the higher stability of the system may be due to higher basicity of the ligand due to inductive effect of the methyl group as well as double bond.

In general, it may be stated that basicities of the monodentate ligands have very little influence on the stabilities of the corresponding UO_2^{++} complexes. Steric factors and ring size presumably determine the metal chelate stabilities with bidentate ligands.

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