

LETTERS TO THE EDITOR

EQUILIBRIUM STUDIES OF MIXED-LIGAND COMPLEXES OF URANYL ION AQUEOUS SOLUTION

In continuation of our earlier studies on Uranyl ion-mixed-ligand complexes in aqueous solution with various carboxylic acids¹⁻⁴, we now present a similar study of UO_2^{2+} -mixed-ligand complexes of systems involving simple as well as substituted aromatic and aliphatic monocarboxylic acids. The experiments were carried out at equal concentrations of metal ion and the ligand acids at $31 \pm 0.1^\circ \text{C}$ and at $\mu = 0.1 \text{ M NaClO}_4$. Earlier studies⁵ and the present work on the uranyl ion-hydrocinnamic acid system revealed that uranyl ion forms only 1:1 complexes with the carboxylic acids chosen for this work.

The preparation of uranyl perchlorate as well as other reagents and their estimations have been given earlier⁵. The carboxylic acids used for this work were all of AnalaR grade and they were standardized with sodium hydroxide solution (0.1 M). The details of apparatus and experimental technique used to obtain the Bjerrum-Calvin titration curves and the methods of calculation of dissociation constants of ligand acids and the stability constants of simple complexes by Irving and Rossotti's method^{6,7} were substantially the same as outlined by Ramamurthi and Santappa.⁵ The system UO_2^{2+} -hydrocinnamic acid was investigated in this work and the dissociation constant of hydrocinnamic acid and the stability constant of 1:1 UO_2^{2+} -hydrocinnamic acid, calculated by Irving and Rossotti's method^{6,7} are reported in Table I. All other values of dissociation constants of acids and stability constants of 1:1 simple complexes were taken from the earlier work⁵, in which they have used identical experimental conditions. The equations employed to calculate the stability constants of the uranyl ion-mixed-ligand complexes were outlined earlier by Ramamurthi and Santappa¹⁻⁴. The stability constants of mixed-ligand complexes, calculated using IBM 1130 computer, are listed in Table I.

From the results we conclude that:

(i) In the case of UO_2^{2+} -formic acid-ligand₂ (the ligand₂ being benzoic, phenyl acetic, hydrocinnamic, phenoxy acetic and *p*-hydroxy benzoic acids), the stability constants of the mixed-ligand complexes are of the order: (ligand₂) hydrocinnamic > phenyl acetic > benzoic > phenoxy acetic > *p*-hydroxy benzoic acid. This is in

accordance with that expected from the basicity of the ligand acids, excepting in the case of UO_2^{2+} -formic-phenoxy acetic acid complex where the higher stability may be attributed to the stabilization through the ether oxygen.

TABLE I

Stability contents of UO_2^{2+} - mixed-ligand complexes.
 UO_2^{2+} as $\text{UO}_2(\text{ClO}_4)_2$; $\mu = 0.1 \text{ M NaClO}_4$; Temperature $= 31 \pm 0.1^\circ \text{C}$

No.	System	Stability constant Log $K_{MLL'}$
1	Uranyl ion-formic-benzoic acid ..	5.06 ± 0.01
2	" -phenyl acetic acid ..	5.13 ± 0.02
3	" -hydrocinnamic acid ..	5.18 ± 0.02
4	" -phenoxy acetic acid ..	4.40 ± 0.02
5	" - <i>p</i> -hydroxy benzoic acid ..	4.25 ± 0.01
6	Uranyl-hydrocinnamic*-benzoic acid ..	6.05 ± 0.01
7	" -phenyl acetic acid	6.16 ± 0.02
8	" - <i>p</i> -hydroxy benzoic acid	5.42 ± 0.01

* Log K_{ML} of Uranyl ion-hydrocinnamic acid complex (1:1) = 3.048. pK_a of hydrocinnamic acid = 4.380.

(ii) In the case of UO_2^{2+} -hydrocinnamic-ligand₂ (ligand₂ being benzoic, phenyl acetic, and *p*-hydroxy benzoic acids), the stability constants of the mixed complexes are of the order: (ligand₂) phenyl acetic > benzoic > *p*-hydroxy benzoic acid, which is obvious from the basicity of the ligands.

The stability constants of these mixed-ligand complexes, involving monodentate ligands only, are of the same magnitude reported for various uranyl ion-monodentate-monodentate mixed-ligand complexes in literature¹⁻⁴.

Dept. of Physical Chemistry, P. V. SELVARAJ.
University of Madras, M. SANTAPPA.
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