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## Note

# INVESTIGATIONS ON $UO_2$–2-METHYL-5-HYDROXY-1,4-NAPHTHALENEDIONE COMPLEX

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There is no report on the affinity of 2-methyl-5-hydroxy-1,4-naphthalenedione to metals. This note concerns its interaction with the uranyl ion in solution at 30°C and in the solid state. pH, spectral and thermal measurements were made.

## EXPERIMENTAL

All the reagents used were of analytical grade. The uranyl nitrate solution was made using distilled water whereas the ligand solution was made up in acetone. The pH titrations in 50% v/v acetone–water medium were performed on a Metrhom Herisau E-520 pH-meter which was calibrated with buffer solutions for the stoichiometry and stability of the system using the Bjerrum–Calvin titration technique [1]. Correction of each pH value due to volume and non-aqueous media according to Van Uitert and Haas [2] was applied. The shapes of the plots (pH vs. volume of NaOH) were as usual.

The modern thermogravimetric balance with Toshniwal furnace was standardised with calcium oxalate. The samples were pyrolysed in air at 10°C $min^{-1}$. A Perkin Elmer Infra Cord spectrophotometer was employed to record the IR spectrum of a nujol mull of the ligand and its complex. THERELEC was used for C, H analysis.

Isolation of the uranyl complex of the title compound was carried out by adding the metal solution to a solution of the sodium salt of the ligand with constant stirring. The red precipitate was filtered, washed many times and dried at 35°C. The theoretical and experimental values for the percentage of carbon and hydrogen in $UO_2(C_{11}H_7O_3)_2$ agreed reasonably well.

| | Calcd. | Found |
|---|---|---|
| C | 40.97 | 41.39 |
| H | 2.17 | 2.70 |

TABLE 1

Stability constants of the $UO_2$-2-methyl-5-hydroxy-1,4-naphthalenedione system

| | Method | | |
|---|---|---|---|
| | A | B | C |
| $\log k_1$ | 9.40 | 9.33 | 9.50 |
| $\log k_2$ | 7.10 | 7.11 | 7.00 |
| $\log k_1/k_2$ | | | 2.5 |
| $\log \beta_2$ | 16.50 | 16.44 | 16.50 |

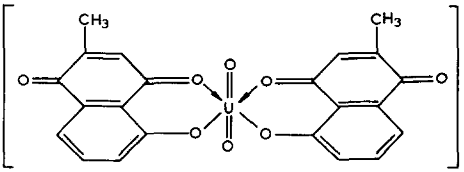
## RESULTS AND DISCUSSION

The proton–ligand stability constant of 2-methyl-5-hydroxy-1, 4-naphthalenedione ($^{P}K^{H}$) was determined from the linear plots of $B$ (pH-meter reading) vs. $\log \bar{n}_H/(1-\bar{n}_H)$, and $\bar{n}_H$ vs. pH. For the metal–ligand stability constants of the system, the formation curves (pH vs. $\bar{n}$) were used, which, on analysis, were found to fulfil the conditions of the Bjerrum half-integral method (A) ($\log k_1/k_2 \geqq 2.5$). Pointwise calculation (B) and graphical (C) methods were also employed for these constants. Reasonable agreement was found between the values of the constants obtained by the different methods (Table 1).

The $\bar{n}$ value for the system nearly reaches 2, indicating the presence of the complexes with 1 : 1 and 1 : 2 stoichiometry in solution. The experimental fact that the curve determined in the presence of the uranyl ion lies below the acid curve points to the participation of the anionic form of the ligand in complexation. Conductometric and chemical analysis also support the pH metric inferences. Low conductance of the complex in acetone ($25.82 \times 10^{-2}$ $ohm^{-1}$ $cm^2$ $mole^{-1}$) pointed to the electrolytic nature of the complex.

The IR study of the compound and its $UO_2(II)$ complex displayed a broad band in the 3400 $cm^{-1}$ range, excepting the spectrum of the $UO_2$ complex, indicating the O–H stretching mode. Another main feature was a marked shift in carbonyl stretching frequency ($>C{=}O$) from 1643 to 1593 $cm^{-1}$ which points to metal–oxygen bonding in the complex.

The structure of the complex consistent with the analytical data is



### *Thermal and kinetic study*

The thermogravimetric curve of $UO_2(C_{11}H_7O_3)_2$ showed its thermal stability up to 40°C, after which its decomposition began and continued up to

TABLE 2

Kinetic data

| Reaction | Eqn. (1) | | Eqn. (2) | |
|---|---|---|---|---|
| | $E$ | $n$ | $E$ | $n$ |
| $UO_2(C_{11}H_7O_3)_2 \rightarrow$<br>$U_3O_8$ + organic matter | 2.01 | 1 | 2.29 | 0.37 |

848°C; a plateau after 848°C corresponded to $U_3O_8$. A slow region from 560 to 615°C, indicating the possibility of the existence of a non-stoichiometric intermediate compound was also noticed.

The non-isothermal decomposition of $UO_2$(II)-2-methyl-5-hydroxy-1,4-naphthalenedione complex was probed kinetically using the Dave–Chopra [3] expressions, eqns. (1) and (2), which have been extensively applied for such studies by Sawhney and co-workers [4–10].

$$k = \frac{(A/m_0)^n(\mathrm{d}x/\mathrm{d}t)}{(A-a)^n} \tag{1}$$

$$\frac{-E/2.303\,R(T^{-1})}{\log(A-a)} = -n + \frac{\log(\mathrm{d}x/\mathrm{d}t)}{\log(A-a)} \tag{2}$$

$A$, $a$ and $\mathrm{d}x/\mathrm{d}t$ were calculated from the derivative thermogravimetric curve derived from the TG curve of the complex by the differential method. Assuming $n = 1$, log $k$ values were collected corresponding to different temperatures using eqn. (1) and plotted against $1/T$; a linear plot, showing that the reaction under study follows first-order kinetics, was observed. For eqn. (2), $(T^{-1})/\log(A-a)$ was plotted against $\log(\mathrm{d}x/\mathrm{d}t)/\log(A-a)$; the straight line relationship with $-E/2.303\ R$ slope and $n$ intercept was obtained. The kinetic data obtained by eqns. (1) and (2) were found to tally (Table 2).

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