COLORIMETRIC STUDIES ON THE REACTION OF U (VI) AND Mo (VI) WITH 3-5-DICHLORO-2-HYDROXYACETOPHENONE AND ITS OXIME

KEEMTI LAL AND S. P. GUPTA

Department of Chemistry, D.N. College, Meerut 250 002, India

ABSTRACT

Chelate formation of uranium and molybdenum with 3, 5-dichloro-2-hydroxyacetophenone and its oxime have been studied. The mole-ratio (M : L) was found 1 : 2. The stability constant of these metal chelates at different ionic strength and their dieclectric constants are calculated.

THE o-hydroxyaldoximes are well known as analytical reagents. Ephraim[1] was first to investigate salicylaldoxime as a reagent for detection and determination of copper. His work was extended by number of other workers. Poddar[2] studied o-hydroxyacetophenone oxime as an analytical reagent and found that this reagent has definite advantages over salicylaldoxime due to the greater thermal stability and increased insolubility of metal complexes.

The formation of complexes of metals with 3, 5-dichloro-2-hydroxyacetophenone oxime have been recently reported by Gupta and Lal[3-4]. The present note describes the colour reactions of uranyl and molybdate ions with 3, 5-dichloro-2-hydroxyacetophenone (HDCA) and 3, 5-dichloro-2-hydroxyacetophenone oxime (HDCAO).

EXPERIMENTAL

Stock solutions of uranyl nitrate and ammonium molybdate (B D.H.), (AnalaR) were prepared in distilled water and their strength determined by usual methods. All other chemicals used were of B.D.H. (A.R.) grade. Buffers of ammonium hydroxide and acetic acid were used to adjust the pH of the solution. The reagents HDCA and HDCAO were prepared as reported earlier[3]. Absorbance and pH measurements were carried out with systronic spectrocolorimeter (type 102) (range 400–700 nm) and pH meter (type 322) respectively.

RESULTS

HDCAO forms instantaneously an orange-yellow coloured, soluble complex with uranyl and molybdate ion. The complex is stable at room temperature. It was observed that the colour of the molybdenum (VI) complex was stable upto 45° C. However, the solution regained its original colour intensity on cooling to room temperature. HDCA also gives a orange-yellow soluble complex with uranyl ion.

The nature of the complexes was studied by the method suggested by Vosburgh and Cooper[5] and found that only one complex was formed under the condition of study in all the systems. The method of continuous variation[6], slope-ratio[7], mole-ratio[8] methods were used in order to establish the molar ratio of metal-ligand. The physical constants of the complexes were calculated using the well known spectrophotometric methods. The results obtained are recorded in Table I.

TABLE I

Physical constant of UO_2 (II) and MoO_2 (II) complexes with HDCAO and HDCA

Metal ion	Colour	λ_{max} (nm)	pH	M : L	Beer's law range ppm	Stability constant ($\mu = 0 \cdot 1$ M)	Sensitivity molar extinction coefficient
Complexation with HDCAO							
UO_2 (II)	orange-yellow	400	7·5–8·0 (7·5)	1 : 2	20–110	5·50	0·55 μg U/cm² 430
Complexation with HDCAO							
UO_2 (II)	orange-yellow	400	6·0–8·5 (7·5)	1 : 2	17–90	6·39	0·33 μg U/cm² 730
MoO_2 (II)	orange-yellow	400	2·5–3·5 (3·0)	1 : 2	2–18	7·28	0·19 μg Mo/cm² 510

(Parentheses value refer to the pH of study).

To study the effect of pH on the complex formation, a large number of solutions were prepared containing the metal and the ligand, the latter being in large excess (15–25 times) in order to obtain maximum colour developments. The spectral readings were recorded at λ_{max} of the complex at various pH values.

Evaluation of Stability Constant :

The stability of the chelates have been calculated by mole-ratio plot, using the relations $K = (1 - \alpha)/4c^2\alpha^3$ and $\alpha = (Em-Es)/Em$ where Em, Es, C and α have the usual significance. With a view to obtaining the thermodynamic stability constant (K) of the chelates, the K at different ionic strength (μ) (NaClO$_4$) studied at suitable pH Table II.

TABLE II

Stability constant of UO_2 (II) and MoO_2 chelates at various ionic strengths (μ)

(Solvent, 75% v/v ethanol-water)

Ionic strength (μ)	log K for UO$_2$ (L$_1$)$_2$	log K for UO$_2$ (L$_2$)$_2$	log K for MoO$_2$ (L$_2$)$_2$
0·15	5·45	6·30	7·20
0·10	5·50	6·39	7·28
0·05	5·53	6·43	7·34
0·02	5·58	6·52	7·41
0·00	5·62*	6·60*	7·90*

* By Extrapolation method.
L$_2$ = HCDAO and L$_1$ = HDCA.

By the method of extrapolation using the log K values, the thermodynamic stability constant and free energy ($\triangle$ F°) at zero ionic strength has also been calculated.

The $\triangle$ F° was found to be 7·73, 9·07 and 10·86 KCal/mole at 27° C, for the chelates UO$_2$ (L$_1$)$_2$, UO$_2$ (L$_2$)$_2$ and MoO$_2$ (L$_2$)$_2$ respectively. HL$_1$ and HL$_2$ are the legands of HDCA and HDCAO respectively.

In order to study the effect of dielectric constant on the stability constant of the chelates, several different percentage of ethanol-water solutions were used. The results are tabulated in Table III,

TABLE III

Stability constants of UO_2 (II) and MoO_2 (II) chelates in Different Ethanol water solvent mixtures

(Ionic strength 0·1 M)

Ethanol (%)	Dielectric constant*	log K for UO$_2$ (L$_1$)$_2$	log K for UO$_2$ (L$_2$)$_2$	log K for MoO$_2$ (L$_2$)$_2$
44·00	51·8C	5·35	6·16	7·04
54·0	46·20	5·40	6·23	7·14
65·0	40·00	5·44	6·32 ·	7·22
75·0	34·00	55·0	6·39	7·27

* Akerlof, G., *J. Am. Chem. Soc.*, 1932, 54, 4125.

DISCUSSION

It is evident from Table I, that metals form orange-yellow colour chelates with HDCA and HDCAO in the stoichiometric ratio of M : L is 1 : 2.

From Table II it can be noted that stability constant of the chelates of molydenum and uranium increases with decreasing ionic strength. The stability constant of the chelates at different percentage of ethanol reveals that the stability constant slightly increases with the decrease in the dielectric constant (ϵ) (Table III) of the media, although the nature of the spectrum does not change with the organic solvent. Optical density increase as the percentage of alcohol increase. In such cases, it is expected that the d'electric constant of the media effect the stability constant of chelate to a great extent. It is noteworthy that an approximate linear relationship is obtained when log K is plotted against $1/\epsilon$.

1. Ephraim, F., *Ber. dt. chem. Ges.*, 1930, 63, 1928 ; 1931, 64, 1210, 1215.
2. Poddar, S. N., *Z. analyt. Chem.*, 1957, 154, 254 ; 1957, 155, 327 ; *Analytica Chim. Acta,* 1963, 28, 586 ; *J. Indian Chem. Soc.,* 1963, 40, 706 ; *Indian J. Appl. Chem.* 1963, 26, 153.
3. Gupta, S. P., Srivastava, S. K. and Lal, K., *Indian J. Chem.,* 1975, 13, 297.
4. Lal, K. and Gupta, S. P., *Curr. Sci.,* 1975, 44, 178.
5. Voshurgh, W. C. and Cooper, G. R., *J. Am Chem. Soc.,* 1941, 63, 437.
6. Job, P., *Ann. Chim.,* 1928, 9, 113.
7. Harrey, A. E. and Manning, D. L., *J. Am. Chem. Soc.,* 1950, 72, 4488.
8. Yoe, J. H. and Jones, A. L., *Ind Eng Anal. Ed.,* 1944, 16, 111,