Studies on the Complex Formation between Uranium and Thiomalic Acid

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Attempts to study the complex formation between thiomalic acid and $UO_2(II)$ has been made using spectrophotometric, potentiometric and magnetic susceptibility measurements. Thiomalic acid gives coloured complexes and has chiefly been used as an analytical reagent.(1-3) Some recent investigations(4-11) on thiomalic acid show it to be a powerful coordinating agent as is expected from the ideal position occupied by the sulphydryl group and two carboxylic groups in the molecule. Thiomalic acid is found to behave as a bidentate ligand with $UO_2(II)$. The complex formed, however, exhibits anamolous magnateic behaviour.

The orangish-yellow coloured complex formed between $UO_2(II)$ and thiomalic acid between pH 3.0~7.0 was studied at a pH 4.5 ± 0.2.

Experimental

Material and Apparatus.—Standard solution of uranyl acetate was prepared from the 'Baker Analysed' $UO_2(C_2H_3O_2)_2 \cdot 2H_2O$ by direct weighing. Fresh solutions of thiomalic acid were prepared by direct weighing whenever needed. pH of the solutions were fixed by sodium hydroxide and hydrochloric acid.

All the spectrophotometric measurements were carried out by means of a 'Unicam' SP 500 spectrophotometer, connected to a 220 V./50 cycles A. C. mains. Absorbance measurements were observed against distilled water blanks. Two lamps, one tungsten filament and the other hydrogen were used for visible and ultraviolet region respectively.

pH titrations were done with a Leeds and Northrup pH meter supplied with all purpose glass electrode operated at 220 V. mains.

Magnetic susceptibility measurements were done by Gouy's method. The assembly consisted of a semi-micro sartorius balance with a Leybold electromagnet. The field obtained was about 5500 gauss with a 2 cm. pole gap.

Experimental Results

Absorbance Studies.—The absorbance of TMA was zero at the wavelength of maximum absorbance of UO_2-TMA complex. The absorbance of UO_2^{2+} was very little at the wavelength of maximum absorbance of the complex, but this could not be neglected. Hence a few blank sets of observations for uranyl acetate solution were taken at different concentrations. These observations were utilized to introduce necessary corrections in the absorbance values for the complex.

TABLE I

Fig. No.	Curve	c $\times 10^3$ M	p	λ_{max}	Vol. of uranyl acetate at the peak	Composition of the chelate $UO_2(II)$: TMA
1	A	4.00	1	390	24.0	1 : 1
	B	2.50	1	390	25.0	1 : 1
	C	2.00	1	390	25.0	1 : 1
2	A	4.00	1	410	25.0	1 : 1
	B	2.50	1	410	25.0	1 : 1
	C	2.00	1	410	24.5	1 : 1
3	A	3.33	1.50	390	20.0	1 : 1
	B	3.33	1.50	410	20.0	1 : 1
4	A	2.22	0.66	390	29.5	1 : 1
	B	2.22	0.66	410	29.5	1 : 1

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The method of Vosburgh and Cooper[12] was employed to determine the nature of the complex formed in solution. Mixtures containing 1 : 0.5, 1 : 1, 1 : 1.5, 1 : 2, 1 : 3, 1 : 4 ratios of uranium(VI) oxide to TMA were prepared, the total volume was kept 50 ml. in each case. Absorbance readings were recorded between a range of 320 mμ to 600 mμ at suitable intervals. The observations when plotted graphically show that the region of maximum absorbance of the solution lies at 390 mμ. Hence only one stable complex is formed under the conditions of study.

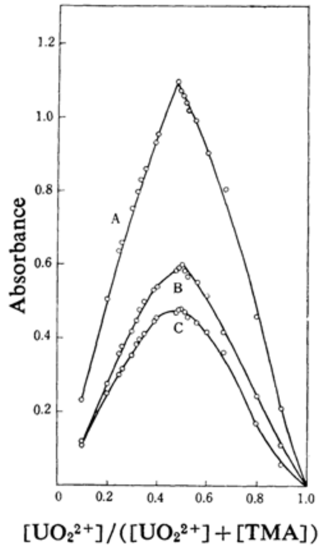

Fig. 1. Absorbance studies of equimolar mixtures of uranyl acetate and thiomalic acid at 390 mμ.
Curve A : Concn. of uranyl acetate, M/250
Curve B : Concn. of uranyl acetate, M/400
Curve C : Concn. of uranyl acetate, M/500

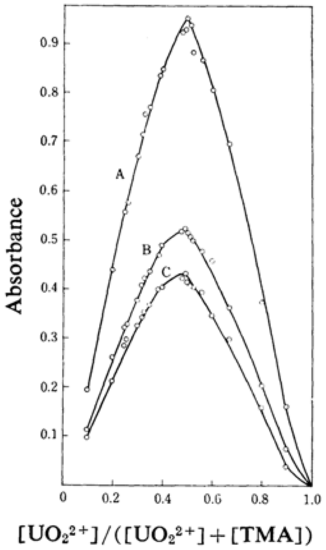

Fig. 2. Absorbance studies of equimolar mixtures of uranyl acetate and thiomalic acid at 410 mμ.
Concentrations is the same as in Fig. 1.

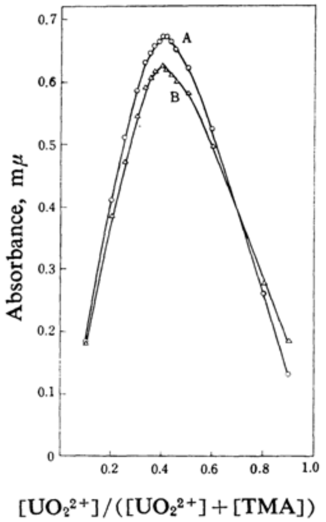

Fig. 3. Absorbance studies of non-equimolar mixtures of uranyl acetate and thiomalic acid.
$p=1.5$
Concn. of uranyl acetate, M/300
Curve A: 390 mμ
Curve B: 410 mμ

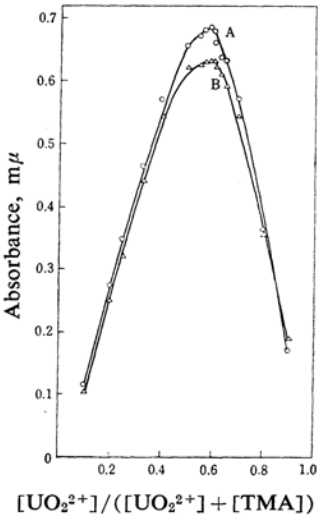

Fig. 4. Absorbance studies of non-equimolar mixtures of uranyl acetate and thiomalic acid.
$p=0.66$
Concn. of uranyl acetate, M/450
Curve A: Wavelength 390 mμ
Curve B: Wavelength 410 mμ

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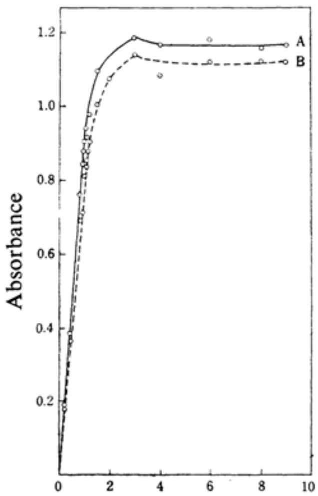
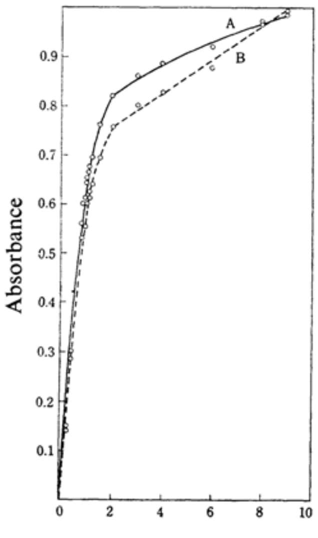
[12] W. C. Vosburgh and G. R. Cooper, *J. Am. Chem. Soc.*, **63**, 437 (1941).

Effect of pH on the Complex.—The absorbances of mixtures containing uranyl acetate and thiomalic acid in the ratio 1 : 3 (each 1×10^{-2}M) at different pH values were observed. It is seen that λ_{max} (390 mμ) of the yellow coloured complex UO_2(II)-TMA remains the same between pH 3.0∼7.0; hence the complex is stable in this range of pH.



Mol. of UO_2(II) per mol. of TMA

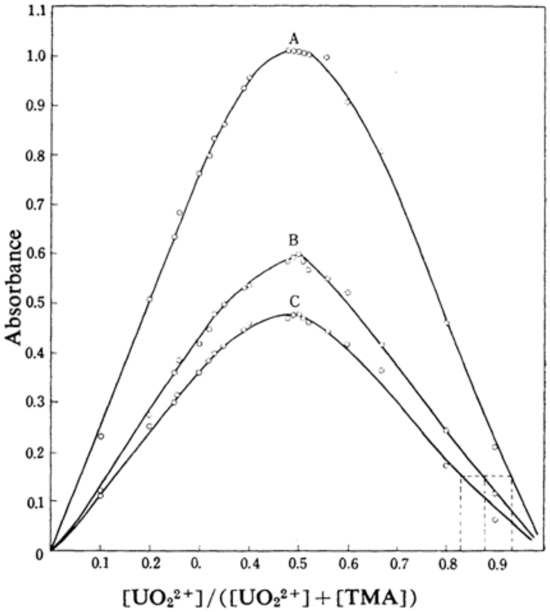
Fig. 5. Absorbance studies of mixtures of uranyl acetate and thiomalic acid by mole ratio method.
Concn. of uranyl acetate, M/300
Curve A : 390 mμ, Curve B : 410 mμ



Mol. of TMA per mol. of UO_2(II)

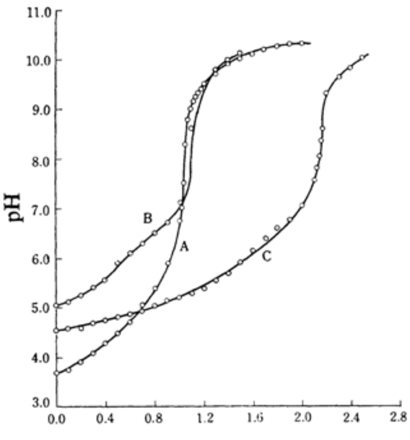
Fig. 6. Absorbance studies of mixtures of uranyl acetate and thiomalic acid by mole ratio method.
Concn. of thiomalic acid, M/400
Curve A : 390 mμ, Curve B : 410 mμ

Stiochiometry of the Components.—The stoichiometric ratio of uranyl to thiomalic acid was determined by the methods of continuous



$[UO_2^{2+}]/([UO_2^{2+}]+[TMA])$

Fig. 7. Evaluation of the stability constant from absorbance measurements.
Concentrations is the same as in Fig. 1.
390 mμ, $p=1$



Volume of NaOH, ml.

Fig. 8. Potentiometric titration curves with a standard alkali.
Concn. of uranyl acetate, M/100
Concn. of TMA, M/100
Concn. of NaOH, M/10
Curve A : 5 ml. TMA+5 ml. KNO_3+100 ml. water
Curve B : 5 ml. uranyl acetate+5 ml. KNO_3 +100 ml. water
Curve C : 5 ml. uranyl acetate+5 ml. TMA +5 ml. KNO_3+100 ml. water

variation[13] and mole ratio[14]. A large number of observations were taken, some of the typical results are plotted in Figs. 1—6.

Table I records the resuls obtained from the method of continuous variation (Figs. 1—4) where '*c*' denotes the concentration of the metal ion and '*c'*' the concentration of the ligand. '*p*' is equal to c'/c.

The 1 : 1 composition of the chelate has been confirmed by the mole ratio method (Figs. 5 and 6).

Stability of the Complex. — The formation constant $\log k$ (at fixed pH and ionic strength) has been calculated from the curves of continuous variation (Fig. 7) using the formula $K=x/\{(a-x)(b-x)\}$, where the symbols have their usual meaning.[14] An average value of $\log k=3.0\pm0.1$ has been obtained. The corresponding free energy of formation ΔF° has been calculated as -4.2 ± 0.2 at 25°C.

Potentiometric Study.—Different solutions of ligand, metal ion and the complex were titrated respectively with a standard solution of sodium hydroxide. The plot between pH values and the volume of sodium hydroxide are shown in Fig. 8.

Magnetic Susceptibility Measurements.—Very dilute solutions can not be utilised for magnetic susceptiblity measurements since additivity law does not hold good at low concentrations. As the solubility of uranyl acetate was not very high, uranyl nitrate BDH Analar grade was used for the preparation of the solution.

$\lambda_{\max}$ of the complex being same in both the cases uranyl nitrate and TMA (0.1 M each) were mixed in the ratio 1 : 1. The susceptibility of this mixture was measured. The results are tabulated in Table II.

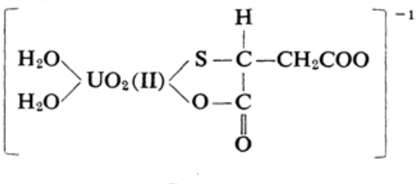
TABLE II

No.	β	Temp., °C	V, ml.	W, g.
1	0.523	32.5	2.589	2.62864
2	0.523	32.5	2.589	2.62984
3	0.523	32.5	2.589	2.62773

No.	ΔW, mg.	$\chi_{\text{sop}}\cdot10^6$	$\chi_{\text{Mcorr}}:10_6$	μ_{eff}, B.M.
1	−3.40	−0.625	739.11	1.34
2	−3.40	−0.624	792.16	1.35
3	−3.31	−0.630	681.71	1.30
	Mean :	1.33		

Discussion

Uranyl usually has a coordination number of four, out of which two appear to be satisfied by thiomalic acid in the complex under investigation. The third hydrogen of TMA is not liberated during complexation, is shown by potentiometric studies in which no shift at the inflexion point is observed, i.e., the amount of sodium hydroxide required at the inflexion point for metal and ligand together is equal to the amount required for the complex. From the spectrophotometric curves of continuous variation and mole ratio, it is clear that the complex formed is 1 : 1. The two remaining coordination positions may assumed to be occupied by water molecules. The magnetic moment of hexavalent uranium should have been zero, however, a moment which is slightly less than that expected for one unpaired electron, is observed. There is a lot of uncertainties about the magnetism exhibited by transuranic elements. There are a many complicating factors, e. g., for many uranium(VI) compounds magnetic moment is sufficiently close to the spin only value for two unpaired electrons to suggest $6d^2$ rather than $5f^2$ arrangement. Moreover, it might be showing a temperature independent paramagnetism which can be confirmed if the observations are taken in a wide range of temperature. Thus the formula of the compound on the basis of the above facts may be written as



Summary

Uranyl ion has been found to form an orange-yellow coloured complex with thiomalic acid. Spectrophotometric measurements reveal a composition of 1 : 1 as UO_2(II) : TMA in the complex, where TMA stands for thiomalic acid. Thiomalic acid is found to behave as a bidentate ligand with UO_2(II) in this complex. This has been concluded by potentiometric method. Magnetic susceptibility measurements, however, show an anomolous magnetic behaviour. The formation constant $\log K$, at fixed pH and ionic strength as calculated from the spectrophotometric curves, comes out to be 3.0 ± 0.1 and the corresponding free energy of formation has been calculated as -4.2 ± 0.2 at 25°C.

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