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COMPLEXES OF TETRAVALENT CERIUM WITH SULPHATE IONS

*N. Hafez **, M.M.El-Dessouky *and M.S.Sayed****

ABSTRACT :

The sulphate - complexes of tetravalent cerium have been studied. Their stability and conditions of their formation solutions has been investigated . In addition the ease of hydrolysis of tetravalent cerium salts in sulphate solutions indicates a lower stability for the monosulphato tetravalent cerium ion . The instability constants of the corresponding complexes were calculated from the results of spectrophotometric measurements . In dilute sulphate solutions of tetravalent cerium the complex cation $[\text{CeSO}_4]^{2+}$ is predominant ; $K_{\text{inst.}} = 2.6 \times 10^{-3}$. When the concentration is raised to 0.05 M mainly the neutral complex $\text{Ce}(\text{SO}_4)_2$ is formed ; $K_{\text{inst}} = 5.9 \times 10^{-3}$. In solutions containing an excess of sulphuric acid , cerium exists mainly as a complex anion.

KEY WORDS

Complexes , Cerium , Sulphates , Analysis.

INTRODUCTION :

The sulphate - complexes of tetravalent cerium have been described as $[\text{CeSO}_4]^{2+}$, $\text{Ce}(\text{SO}_4)_2$, $[\text{Ce}(\text{SO}_4)_2]^{2-}$ and $[\text{Ce}(\text{SO}_4)_4]^{4-}$ [1-6] . The published information concerning their stability and conditions of their formation does not agree with the behaviour of cerium in sulphate solutions .

The instability constants of $\text{Ce}(\text{SO}_4)_2$ ion is given as 5.7×10^{-4} and 2.8×10^{-4} by (3,4). In addition the ease of hydrolysis of tetravalent cerium salts in sulphate solutions indicates a lower stability for the monosulphato tetravalent cerium ion . The conditions of formation , composition and stability of sulphatocerium complexes in aqueous solutions are reported [3,4] . Electrophoresis has been used to determine the composition of the complex ions and their charges . The instability constants of the corresponding complexes can be calculated from the results of spectrophotometric measurements .

* : Egyptian Armed Forces.

** : Hot Laboratory , Atomic Energy Authority , Cairo , Egypt.

*** : Hot Laboratory , Atomic Energy Authority , Cairo , Egypt.

EXPERIMENTAL :

All the reagents used were of analytical grade . Cerium sulphate and trivalent cerium perchlorate were prepared from cerium ammonium nitrate as described [6,7] . Tetravalent Cerium perchlorate was prepared by electrolytic oxidation of trivalent cerium perchlorate using an two platinum electrodes with voltage difference of 10-12 volts(>2.48) and electric current of 2.5 A for 4h[8].The degree of oxidation was 89%after their quantitative determination spectrophotometrically. In the electrolysis a potentiometric arrangement was applied which allows the voltage for the limiting current to be increased . An increase in the electric current is undesirable because it heats the solution . The electrolysis was carried out at 2.0 - 2.5 A and 10 - 12 V for 45 min. At the end of the experiment the cerium content in the catholyte and the anolyte were determined volumetrically by titrating with a solution of Mohr's salt using phenylanthranilic acid . The results are given in Tables 1 and 2 .

RESULTS AND DISCUSSION :

In studying equilibrium in sulphuric acid solutions the measurements are made at $\lambda = 315 \text{ nm}$ because at this wavelength the absorption by sulphuric and perchloric acids can be neglected as shown in Fig.1 . Fig.2 shows results obtained by the isomolar series method with different total concentrations of the reacting components . As the total concentration of reacting components is increased , the maximum absorbance is displaced .

At concentrations $[\text{CeIV}] + [\text{SO}_4]^{2-} = 0.002 \text{ M}$, the $[\text{Ce SO}_4]^{2+}$ cation is dominant . With $[\text{CeIV}] + [\text{SO}_4]^{2-} = 0.005 \text{ M}$, mainly $\text{Ce}(\text{SO}_4)_2$ is formed . The instability constant of $[\text{CeSO}_4]^{2+}$ ion , calculated from the isomolar series results, is 1.3×10^{-3} . A study of displacement from the equilibrium when the concentration of one of the components is kept constant while the other varies to allow to determine the composition of the complex and its stability with high accuracy .

Results from measurments on tow series of solutions are shown in Fig.3 . With a constant sulphat ion concentration and varying tetravalent cerium concentration. Results showed that the $[\text{CeSO}_4]^{2+}$ is formed at concentration ratio greater than 2, but is considerably dissociated as indicated by the absence of a sharp inflection on the curve for variation of absorption with component concentration ratio .Table 3 gives the results of calculating the approximate instability constant of the $[\text{Ce SO}_4]^{2+}$ complex from the formula :

$$K = \frac{C_1 C_2 (P-1)}{C_2 - C_1(P)}$$

where: C1 and C2 are the ligand concentration for two experiments corresponding to which the absorbance are A1, A2 and $P = A2 - A1$.

Results from measurements on two series of solutions are shown in Fig. 4 with constant cerium concentration and varying sulphate concentration. The results indicated that the cerium is completely combined in a complex only when there is a considerable excess of sulphate ions in solution. The number of coordinate (SO_4)²⁻ group from the results of our experiments coincides with the published data and also the neutral complex $\text{Ce}(\text{SO}_4)_2$ is formed under the same conditions. The calculated values of its instability constants are given in Table 4. For both series the ionic strength of solution was measured and kept.

REFERENCES:

- 1- T.W. Newton and G.M. Arcand ; J. Amer. chem. Soc., 75, 2449 (1963) .
- 2- R.E. Connick and S.W. Mayers ; J. Amer. Chem. Soc., 73, 167 (1970) .
- 3- R.E. Moore and R.C. Anderson ; J. Amer. Chem. Soc., 67, 167 (1965).
- 4- T.J. Hardwick and Robertson ; Canad. J. Chem. , 29, 828 (1961).
- 5- V.A. Korobova , G.R. Prik ; Russ. J. Inorg. Chem., 10, (4) (1965) .
- 6- M.E. Hafez , H.M. Rowshdy , N. Hafez ; J. Radioanal. Chem., 45, 277 (1980) .
- 7- M.E. Hafez , N. Hafez ; J. Radioanal. Nucl. Chem. letters. , 166, (3) 203-216 (1992) .
- 8- S. Prakash , G.D. Tuli , S.K. Basu , R.D. Madan , Advanced Inorganic Chemistry , S. Chand & Company Ltd. , Ram Nagar , New Delhi , (1987).

Table 1: Migration of cerium ions in sulphate solutions

Table 3 . Instability constant of the $[\text{CeSO}_4]^{2+}$

C1	C2	A1	A2	P	K
0.38×10^{-2}	1.76×10^{-2}	0.114	0.187	1.64	3.1×10^{-2}
1.73×10^{-2}	2.64×10^{-2}	0.187	0.232	1.24	2.4×10^{-3}
2.64×10^{-2}	3.52×10^{-2}	0.232	0.270	1.16	8.2×10^{-3}
8.52×10^{-2}	4.40×10^{-2}	0.270	0.290	1.07	5.7×10^{-2}
					2.6×10^{-2}

Table 4. Instability constants of the CeSO_4 complex

C1[M]	C2[M]	A1	A2	P	K
5×10^{-2}	1×10^{-2}	0.267	0.377	1.41	6.9×10^{-2}
1×10^{-2}	2×10^{-2}	0.377	0.466	1.23	5.9×10^{-2}
2×10^{-2}	3×10^{-2}	0.466	0.494	1.07	4.8×10^{-2}
					5.9×10^{-2}

Table 1: Migration of cerium ions in sulphate solutions

no.	serium salt concentration [M]	concentration of H ₂ SO ₄ [M]	mohr's salt solution [ml]	
			catholyte	anolyte
1	0.025	0.3	0.4	2.09
2	0.025	0.5	0.2	4.30
3	0.025	1.0	0.3	3.70
4	0.025	2.0	0.8	4.10
5	0.025	4.0	0.2	4.30
6	0.025	6.0	0.5	3.80
7	0.025	8.0	0.3	3.50
8	0.0125	2.0	0.6	4.40
9	0.0125	4.0	0.4	4.30
10	0.0125	6.0	0.8	4.50
11	0.0030	1.0	0.2	2.50
12	0.0030	2.0	0.7	2.80
13	0.0030	4.0	0.9	3.20

Table 2: Migration of cerium ions in perchlorate solutions in the presence of Na₂SO₄

EXP.	concentration of serium salt	Na ₂ SO ₄ concentration	mohr's salt [ml]	
			catholyte	anolyte
1	1.02×10^{-2}	0.98×10^{-2}	2.10	0.80
2	2.00×10^{-3}	3.00×10^{-3}	2.80	2.20
3	1.089×10^{-2}	3.23×10^{-2}	2.3	2.10

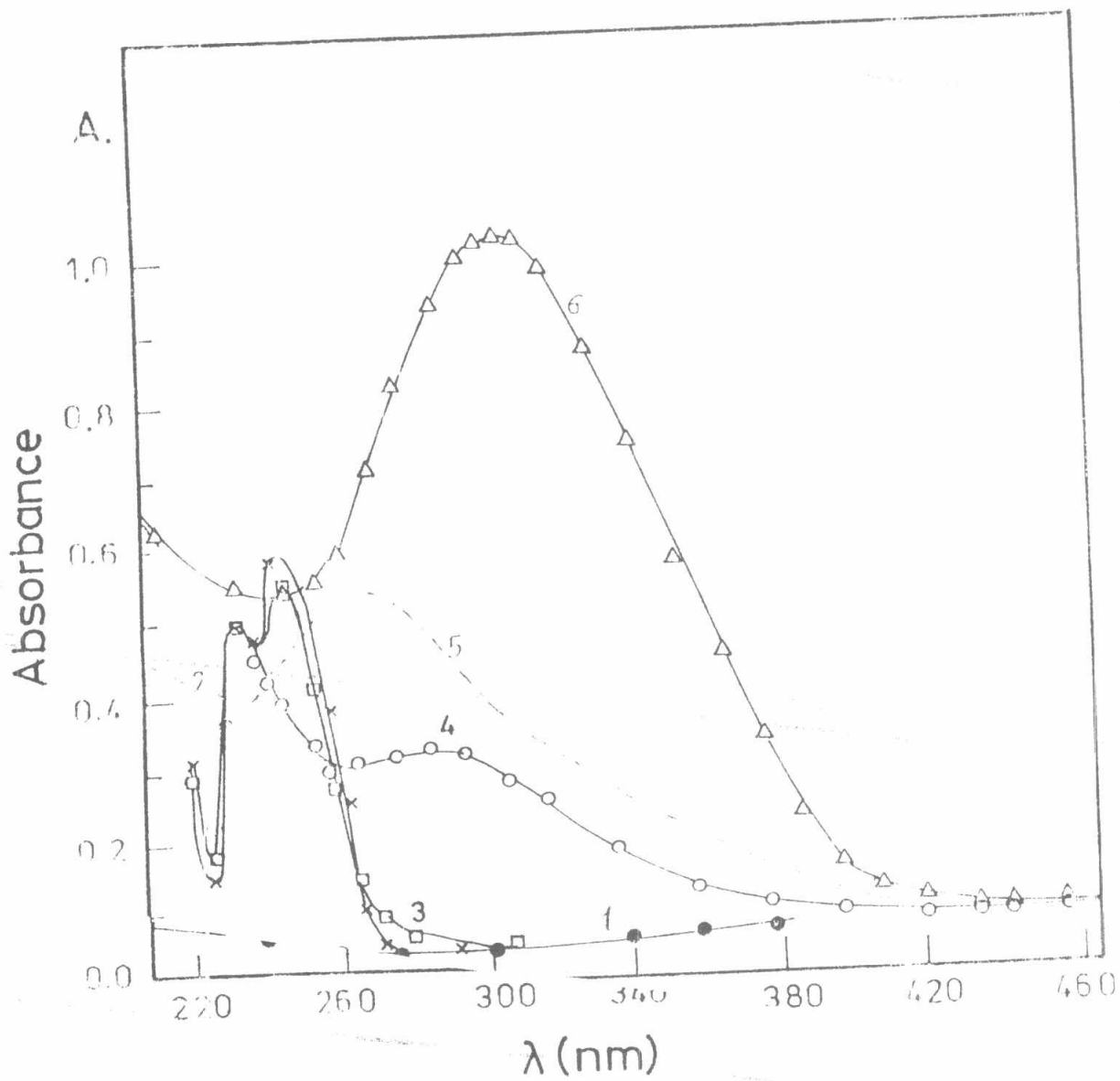


FIG. 1 Light absorbance spectra of Ce (III) , Ce(IV) in sulphate and sulphate complex .

- (1) H₂SO₄ 1N
- (2) Ce (ClO₄)₃ in 1N HClO₄
- × (3) Ce₂(SO₄)₃
- (4) Ce₂(SO₄)₃ in 1N H₂SO₄
- - - (5) Ce (SO₄)₂
- △ (6) Ce (SO₄)₂ in 1N H₂SO₄

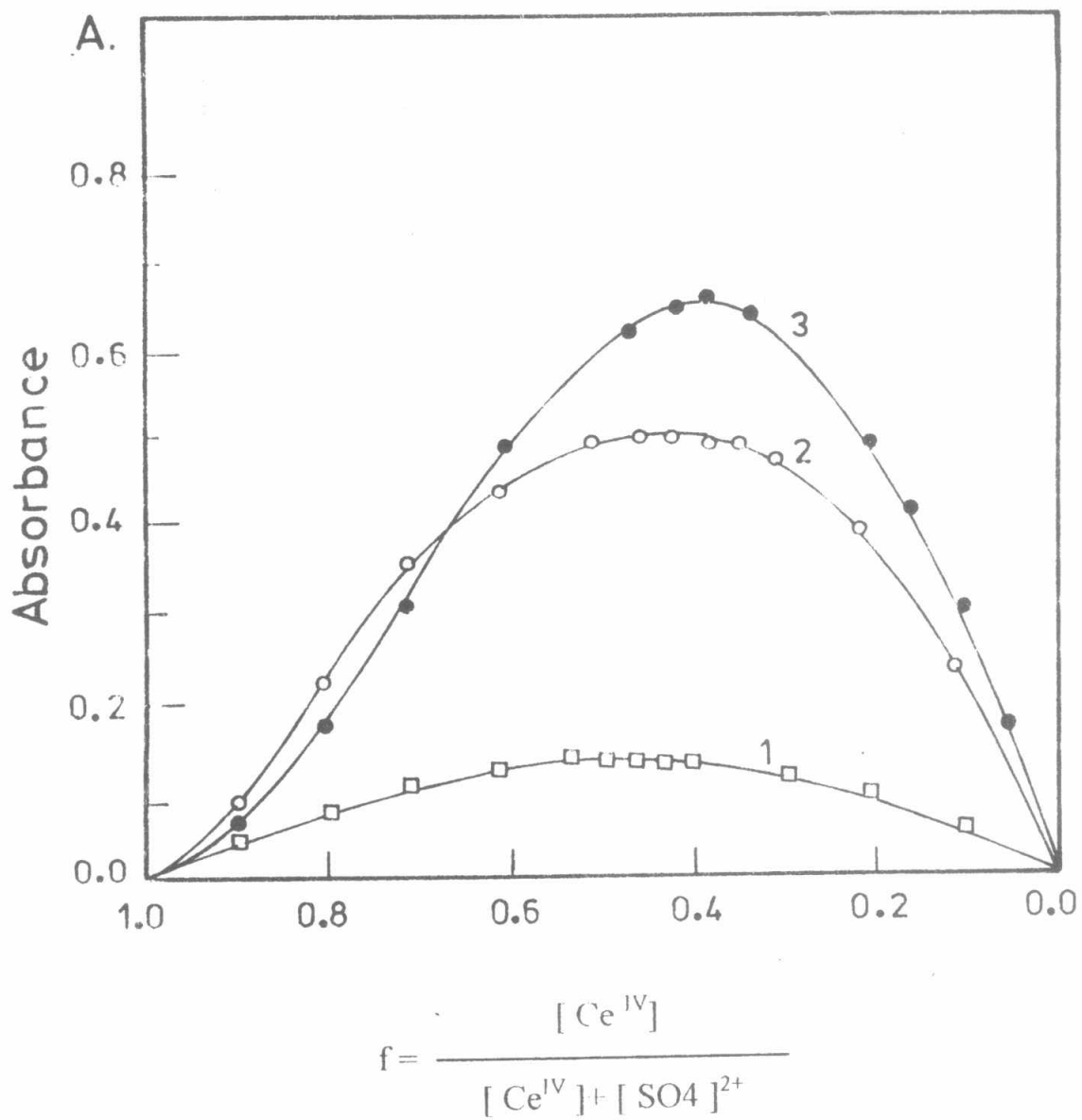


FIG. 2 Isothermal series

- $[\text{CeIV}] + [\text{SO}_4^{2-}] = 0.002 \text{ M}$ λ 315nm.
- $[\text{CeIV}] + [\text{SO}_4^{2-}] = 0.005 \text{ M}$ λ 315 nm..
- $[\text{CeIV}] + [\text{SO}_4^{2-}] = 0.051 \text{ M}$ λ 315 nm.

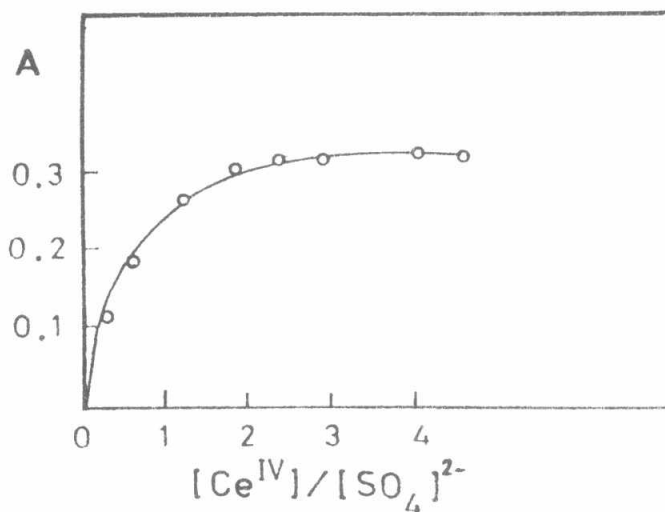


FIG 3: Chang in the absorbance [A] of the solution with constant sulphate ions concentration and varying CeIV ion concentration.
 $\lambda = 315 \text{ nm}$, $[SO_4]^{2-} = 0.003 \text{ g ion / lit}$.

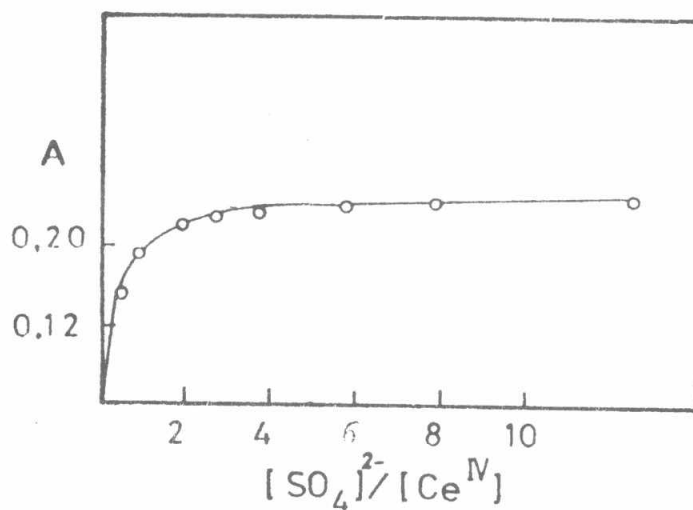


FIG 4: Chang in the absorbance [A] of the solution with constant Ce(IV) ion concentration and varying sulphate ion concentrations.
 $[Ce(IV)] = 0.001 \text{ g ion / lit}$, $\lambda = 315 \text{ nm}$.