RADIATION RESEARCH 13, 641–643 (1960)

A Study of the Extinction Coefficient for Ferric and Ceric Ions

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INTRODUCTION

Although there are many published values for the extinction coefficient of ferric ion and ceric ion in sulfuric acid solution, it was felt desirable, in view of their widespread use in radiation dosimetry, that the values of the extinction coefficients and the effects of temperature and acid concentration should be redetermined.

RESULTS

The stated error in the extinction coefficients was found by combining as random errors a standard deviation with a calibration and a weighing or titration error.

Ferric Species

Standard ferric sulfate solutions were prepared by dissolving spectrographically pure iron rod (Johnson Matthey) in sulfuric acid and oxidizing with hydrogen peroxide. The decadic molar extinction coefficient of ferric ion in 0.8 N sulfuric acid at 24.9°C was found to be 2199 $\pm$ 4 liters mole^{-1} cm^{-1} at 304 mμ. The effect of a decrease of acidity and of added ferrous and cupric sulfates at this temperature is shown in Table I. Values of the ratio of observed extinction coefficient to the extinction coefficient in 0.8 N sulfuric acid are given.

The temperature coefficient was measured in the range 20° to 30°C. for solutions of ferric ion in 0.8 N and 0.1 N sulfuric acid and in 0.01 N acid containing 0.01 M cupric ion. The results are given in Table II.

Ceric Species

Ceric sulfate solutions were prepared by dissolving reagent-grade ceric sulfate (G. F. Smith) in very dilute ceric sulfate solution (approximately 0.05 M in 0.8 N H_2SO_4) and determining the concentration by titration against arsenious oxide (*1*). The molar extinction coefficient of ceric ion in 0.8 N sulfuric acid was measured at 320 mμ and found to be 5565 $\pm$ 15 liters mole^{-1} cm^{-1}. In 0.1 N sulfuric acid the

TABLE I

EFFECT OF DECREASE OF ACIDITY AND OF ADDED FERROUS AND CUPRIC SULFATE ON THE EXTINCTION COEFFICIENT OF FERRIC ION AT 24.9°C

Normality H_2SO_4	0.8	0.1	0.01	0.8	0.1	0.1	0.01	0.01	0.01
Concentration $FeSO_4$	—	—	—	0.01	0.001	0.01	0.01	—	0.001
Concentration $CuSO_4$	—	—	—	—	—	—	—	0.01	0.01
Relative extinction coefficient	1.000	1.006	0.905(7)	1.004	1.017	1.055	1.115	0.981	0.986

TABLE II

TEMPERATURE COEFFICIENT OF EXTINCTION COEFFICENT OF FERRIC ION—EFFECT OF DECREASE OF ACIDITY AND OF ADDED CUPRIC SULFATE

0.8 N H_2SO_4	0.7%/°C
0.1 N H_2SO_4	0.6%/°C
0.01 N H_2SO_4 + 0.01 M Cu^{2+}	1.1%/°C

extinction coefficient was somewhat less, being only 0.938 of the value in 0.8 N acid.

The extinction coefficient of cerous ion in 0.8 N sulfuric acid was also determined and found to be 2.7 ± 0.2 at 320 mμ; 24.4 ± 2.4 at 305 mμ; and 26.4 ± 2.5 at 304 mμ.

DISCUSSION

The extinction coefficient for ferric ion agrees with previously published values (*2–4*), as does the effect of acidity (*5*, *6*). The temperature coefficient in 0.8 N acid is also in agreement with the values in the literature (*5*, *7–9*), but the temperature coefficient in 0.1 N acid differs from the previously reported value (*5*). The effects of ferrous and cupric sulfates on the apparent extinction coefficients of ferric sulfate are of practical importance because there are many instances in chemical dosimetry of radiation of both low and high linear energy transfer in which it is necessary to measure changes in ferric sulfate concentration in solutions containing one or both of the other sulfates in concentrations lying in the ranges given in Table I.

In the case of cerium, although there are several values of the extinction coefficient (10–12) that are in agreement, none of them have an error assigned to them. In the present work the extinction coefficient agrees with the published values, but the effect of acidity is less than has been reported (*13*). The use of the ceric sulfate system in chemical dosimetry has been reviewed recently (*14*, *15*).

Since this work was carried out, further confirmation of the values for the extinction coefficient of both ferric and ceric ion has appeared (*16*, *17*).

The extinction coefficient of cerous ion at various wavelengths is a correction which must be taken into consideration when the extinction coefficient for ceric

ion is determined by comparison with that for ferric ion. The present value agrees with one reported previously (*4*).

ACKNOWLEDGMENT

* Grateful acknowledgment is made of help and advice from Professor F. S. Dainton in preparing this manuscript, which was completed after the death of Dr. Miller.

RECEIVED: November 21, 1959

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