A SPECTROPHOTOMETRIC STUDY OE ZIRCONIUM COMPLEXES OF 4, 5-DIHYDROXYFLUORESCEIN

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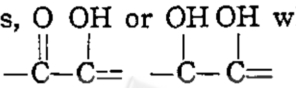
Zirconium (IV) ions form violet red complex with 4,5-dihydroxyfluorescein in fairly strong mineral acid medium. The reagent has been successfully applied as a metal indicator in the direct EDTA titration of zirconium.

The complex formed by 4,5-dihydroxyfluorescein and zirconium ions has been studied spectrophotometrically in $0.1\,M$ HCl solution. It is found that when an excess of metal ion is present, a violet red colored complex with metal-ligand ratio of 1:1, (MR) is formed and when an excess of 4,5-dihydroxyfluorescein is present a 1:2 complex (MR_2) may be predominant. The 1:1 complex has maximum absorption at $510\,m\mu$ and the 1:2 complex has very low solubility and tends to precipitate out from the solution. Job's method, log-ratio method and gravimetric method were used to establish the composition of complexes. The apparent stability constant of the 1:1 complex is found to be log $K_h=4.46$ or $K_h=2.9\times10^4$ at pH 1.2.

INTRODUCTION

As the importance of zirconium grows in the fields of chemistry and metallurgy, the literature of analytical chemistry continues to show evidence of a vivid interest in the determination of zirconium. A number of analytical methods for zirconium have been proposed recently.[1,2] These are covered in gravimetric, volumetric, spectrophotometric, spectrographic and x-ray fluorimetric methods. The nuclear characteristics of zirconium allow it to be determined also by radiochemical and activation methods. Among these analytical methods, spectrophotometric methods offer the most convenient way for the determination of a small amount of zirconium. So far a variety of organic reagents has been used as chromogenic reagents for the spectrophotometric determination of zirconium. For examples, arizarin red S, morin, quercetin, chloranilic acid, phenylfluorone, thorin, xylenol orange, pyrocatechol violet, methylthymol blue, gallocyanine MS, arsenazo III; stilbazogall II, chrome azurol S., nitrosulfophenol S and picramine R are the more common reagents.[1,2]

In examing these reagents, one can find that a trend of preferred colorimetric and fluorimetric reagents for zirconium is to contain the groups,



$-\overset{\overset{O}{\|}}{C}-\overset{\overset{OH}{|}}{C}=$ or $-\overset{\overset{OH}{|}}{C}-\overset{\overset{OH}{|}}{C}=$

which permit the formation of a stable five-membered ring with zirconium replacing one or two hydrogens.

Since 4, 5-dihydroxyfluorescein has both of these two groups in its structure, it was found that the reagent forms stable violet red complex with zirconium in fairly strong mineral acid medium. Based on this fact, the author successfully applied it as metal indicator in the direct EDTA titration of zirconium.[3]

For the better understanding of this color formation, it is of interest to investigate the complex formed by 4, 5-dihydroxyfluorescein and zirconium ion in aqueous solution spectrophotometrically.

EXPERIMENTAL

REAGENTS

4, 5-Dihydroxyfluorescein:—4, 5-Dihydroxyfluorescein, pyrogallolphthalein (The British Drug Houses Ltd., England) was purified by dissolving the dye in 95% ethanol and pouring the solution into larger amount of water to recrystallize it. The recrystallized dye was dried in a vacuum desiccator at room temperature. A $10^{-3}M$ ethanol solution used in the experiment was prepared by dissolving an appropriate amount of the dried recrystallized dye in 95% ethanol.

Standard Zirconium Solution:—A $10^{-2}M$ solution in $1\,M$ hydrochloric acid was prepared by dissolving an appropriate amount of reagent grade $ZrOCl_2 \cdot 8H_2O$ (Wako Pure Chemical Ind. Ltd., Japan) in 1:1 aqueous hydrochloric acid and diluting it with water. The concentration of zirconium was determined by EDTA titration using xylenol orange as indicator. More diluted zirconium solutions were prepared by diluting the above standard solution with $1M$ HCl solution.

All other chemicals used in the experiment were of analytical reagent grade.

APPARATUS

The absorption measurements were made with a Beckman Model DU spectrophotometer using matched silica cells of 10 *mm* optical path. A Horiba *p*H meter, Model M-4E, with a pair of glass and calomel electrodes was used for all *p*H measurements.

METHOD and RESULT

The Color Formation Between 4, 5-Dihydroxyfluorescein and Zirconium Ion.

The reagent, 4, 5-dihydroxyfluorescein in $0.1\,N$ HCl solution is golden yellow in color. When a small amount of zirconium is added to the reagent solution, it turns into violot red color and finally the precipitation occurred. But in the presence of large amount of zirconium ions no precipitation is formed even being allowed to stand for several hours. On the contrary, the treatment of acidic solution of zirconium with an alcoholic solution of 4, 5-dihydroxyfluorescein solution, a violet red coloration occures at first. The violet red color becomes deeper with increasing the concentration of 4, 5-dihydroxyfluorescein. As the 4, 5-dihydroxyfluorescein concentration is increased still further, a point is reached where the precipitation of complex begins. These facts indicate two kinds of complexes may exist.

Absorption Spectra of 4, 5-dihydroxyfluorescein and its Zirconium Complex.

In order to understand the nature of coloration, the absorption spectra of 4, 5-dihydroxyfluorescein and its zirconium complexes are investigated. Figure 1 shows these absorption curves.

The reagent, 4, 5-dihydroxyfluorescein shows an absorption maximum at 460 *mμ*, while the Zr—4, 5-dihydroxyfluorescein system shows maximum at 510 *mμ*. Since zirconyl chloride exhibit no appreciable absorption in the range of 460 *mμ* to 510 *mμ*, the shift of the absorption maximum may indicate the formation of Zr—4, 5-dihydroxyfluorescein chelate. The effect of time on color formation was also investigated. The absorbance becomes constant after 10 minutes of mixing and it is stable over a three-hour period under ordinary laboratory condition.

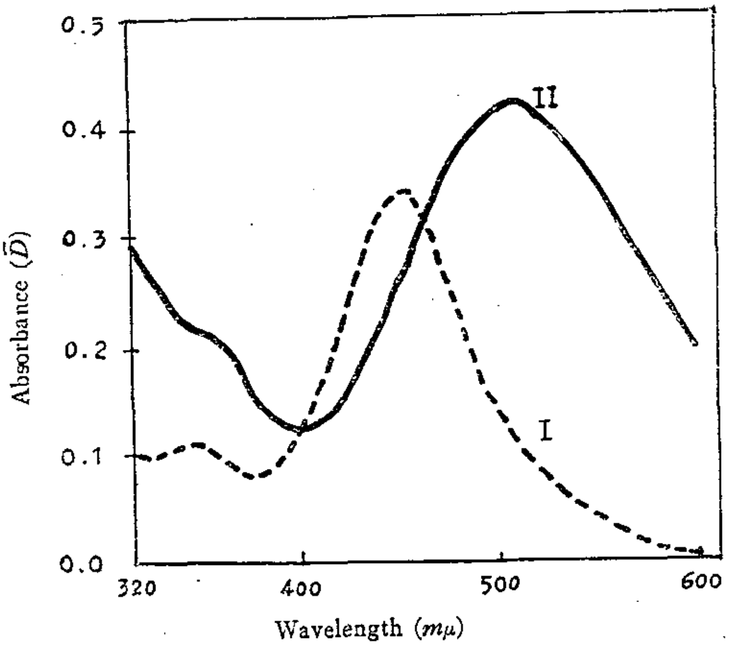


Fig. 1. Absorption Curves of 4,5-Dihydroxyfluorescein and Its Zirconium (IV) Complex at *p*H 2.0.
Curve I : $8.0\times10^{-5}M$ 4,5-Dihydroxyfluorescein
Curve II: $8.0\times10^{-5}M$ 4,5-Dihydroxyfluorescein
$2.4\times10^{-4}M$ Zirconium (IV)

The Composition of Complex.

Job's method of continuous variation was used to examine the composition of the complexes. Absorbances were measured for a series of solutions containing varying mole fraction of metal and 4, 5-dihydroxyfluorescein, their sum remaining constant. The results are shown in Figure 2.

The Job's plots show a maximum at 0.5 and also there is an indication of a discontinuity at 0.67. It indicates that at lower *p*H around 1.0 and in the excess of metal ion the 1:1 complex (MR) is formed and at higher *p*H and in the excess of 4, 5-dihydroxyfluorescein the 1:2 complex (MR_2) may be predominant.

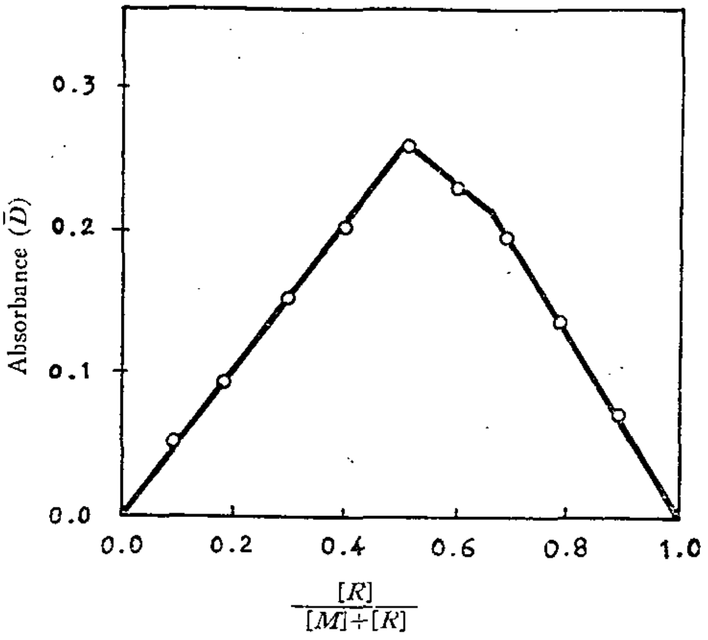


Fig. 2. Job's Continuous Variation Plot for 4,5-Dihydroxyfluorescein—Zirconium System in 0.1 M HCl and 10% Ethanol.
$[M]+[R]=0.98\times10^{-5}M$ $\lambda=500\ m\mu$

The 1:2 complex, MR_2 is unstable in the solution and tends to precipitate out in the presence of excess of dye. Because of its low solubility, it is difficult to study spectrophotometrically. Alternatively the precipitate was prepared and its composition was determined by gravimetric method. The precipitate was ignited to ZrO_2 and the dye to zirconium ratio in the compound was found to be 2 to 1.

Determination of Stability Constant by Log-Ratio Method.

Since the 1:2 complex of zirconium and 4,5-dihydroxyfluorescein has very low solubility in water, only the stability constant of 1:1 complex was determined by the log-ratio method proposed by Diehl and Lindstrom.[4]

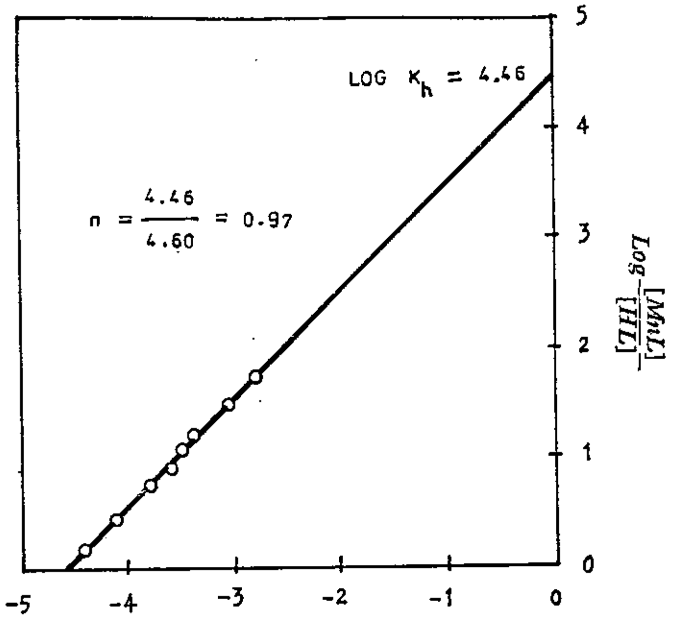
Because the determination of stability constant is carried out at *p*H 1.2 and the acidic nature of hydroxy group of the ligand is very weak, so that its proton is released on chelation. The apparent stability constant of complex at a given *p*H's, K_h is related to the following equation in the *log*-ratio method,[4] that is

$$log\frac{[MnL]}{[HL]}=n\ log[M]+log\ K_h$$

The plot of $log[MnL]/[HL]$ vs. $log[M]$ gives the straight line with slope n, the combining ratio and intercept, K_h.

The experimental work was carried out with a series of the solution containing the same total concentration of $3.93\times10^{-5}\ M$ 4,5-dihydroxyfluorescein and the different concentration of zirconium ion at constant *p*H of 1.2 at 30°C±1°.

The results were shown in Figure 3.



Log [*M*]

Fig. 3. Log-Ratio Method Plot for Zirconium and 4,5-Dihydroxyfluorescein System at *p*H 1.2, μ=0.1, λ=500 $m\mu$ and 30°*C*

The combining ratio obtained by the *log*-ratio method was found to be 0.97 indicating one to one chelate is formed at the given condition. The apparent stability of one to one chelate formed by 4, 5-dihydroxyfluorescein and zirconium ion is found to be *log* K_h=4.46 or K_h=2.9×10^4 at *p*H 1.2.

DISCUSSION

The hydrochloric acid medium was selected for the present study with following reasons;

a) Hydrochloric acid is preferred to perchloric acid, because of greater stability of zirconium in hydrochloric acid solution.[5)]

b) Nitric acid is inferior to hydrochloric acid, because of its tendency to oxidize the dye., especially in the solution of greater acidity and at elevated temperature.

c) Sulfuric acid medium is not desired because of the complexing action of sulfate with zirconium.

Zirconium forms polymerized species readily and the rate of the formation of these species is dependent on the concentration of zirconium ions, the anions associated with zirconium, the *p*H, the temperature and the time of standing after dissolution.[6)] Because of the complexity of aqueous zirconium solution, the published data on the complexes of zirconium often give conflicting evidence as to their composition. The complexes formed by zirconium and xylenol orange, XO is an example.[7)] Babko and Shtokalo reported a 1:1 XO-zirconium complex in 1 *N* hydrochloric acid and a 2:1 complex at *p*H 2.

Budesinsky postulates a complex with 2 moles of zirconium per 1 mole of XO. Cheng reports 1:1 complex in 0.2-1.0 N perchloric acid media, but also suggests the complexes may have some other composition when excess of XO is present.

Champion and his coworkers conclude that when excess of metal is present a complex with XO:metal ratio of 1:1 is formed and when excess of xylenol orange is present (*i.e.*, XO:metal$\geq$2) a 2:1 complex is formed which does not undergo further reaction.

The same discrepancy is observed between present result and that of Kekedy and Balogh.⁸⁾ They reported the ratio of 4, 5-dihydroxyfluorescein to zirconium is 2 to 3 in HNO_3 solution at pH 2.3.

ACKNOWLEDGEMENT

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