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# A SPECTROPHOTOMETRIC STUDY OF THE HYDROLYSIS OF URANYL ION

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Edited by E. L. Brady

* * *

March 1, 1946

This report is to be included in the Plutonium Project Record with the collected papers of Volume XI, and is not available for publication elsewhere.

Date Received: June 13, 1946
Date Issued: June 14, 1946

## ABSTRACT

A spectrophotometric study of the behavior of uranyl solutions of concentrations from 0.004 M to 0.16 M and pH values between 2.00 and 4.30 has been made. The absorption spectrum of $UO_2^{++}$ is assumed to be given by studies at pH 2. Beer's Law is obeyed at this pH.

The fit of the data obtained to the dimerization equation proposed by Best, Taub, and Longsworth,

$$2\ UO_2^{++} + H_2O \rightleftharpoons UO_3 \cdot UO_2^{++} + 2\ H^+$$

has been investigated. It is found that the above reaction, with a mass action constant, $K = 1.35 \times 10^{-6}$, does not adequately explain the results under conditions of advanced hydrolysis.

# A SPECTROPHOTOMETRIC STUDY OF THE HYDROLYSIS OF URANYL ION

In the course of study of the solution physical chemistry of hexavalent uranium and its complexes, it became apparent that the hydrolysis of uranyl ion deserved considerable attention. The color of a uranyl solution deepens with increasing basicity, and therefore, optical methods of analysis show promise. The spectrum was explored in great detail as a function of pH and uranyl concentrations over the range of wavelengths from 210 mμ to 500 mμ, as discussed in the work below. Previous work by Best, Taub, and Longsworth[1] was re-examined critically and correlation of the conclusions with these studies was attempted.

## Experimental

The spectrophotometer used was the Beckman Quartz Spectrophotometer, which gives a minimum band width of approximately one millimicron (never more than two) over the range from 210 to 1000 mu. Quartz absorption cells ranging in length from 0.5 to 10 cm are used in an effort to keep the optical density between 0.1 and 1 since values below 0.1 are inaccurate and above 1 are found to be questionable due to the scattered light in the instrument. The Beckman Laboratory Model pH Meter was used for the determination of pH values.

Uranyl perchlorate was prepared by fuming uranyl nitrate repeatedly with perchloric acid and then finally fuming off most of the excess perchloric acid and diluting to a convenient concentration. It was also prepared by adding an approximately equivalent amount of concentrated perchloric acid to a weighed sample of uranyl oxide[2]. The $UO_3$ was prepared according to the directions of Best, Taub, and Longsworth by precipitation of uranyl peroxide, ignition of the washed solid, suspension of the ignited solid several times in water, followed finally by ignition to obtain an anhydrous product. The $HClO_4$ solutions of $UO_3$ were made up to a convenient concentration and analyzed for uranium content by gravimetric analysis.

Solutions for spectrophotometric study were then made up by taking aliquots of the stock solution, diluting to the proper concentration and adjusting to the desired pH by adding 6 N sodium hydroxide or concentrated perchloric acid. Many of these solutions were again checked for concentration and pH after the absorption curve had been taken.

Results

Preliminary absorption curves were obtained using Mallinckrodt uranyl nitrate over the concentration range $2x10^{-3}$ to $4x10^{-5}$ M in order to determine workable concentration and wavelength ranges. No attempt was made to control the pH of these solutions. These curves soon made it clear that the uranyl nitrate system is not a simple one, since agreement with Beer's Law was not obtained. The curves showed a weak peak at about 410 mμ, a minimum at 370 mμ, a pronounced rise, with a shoulder at about 305 mμ, to a very strong absorption in the ultra violet rising rapidly at about 250 mμ. There seemed to be a peak at around 225 mu. Attempts to determine the molar extinction coefficient of this peak by investigating more dilute solutions showed that the "peak" was not within the wavelength range of the instrument and that the apparent decrease beyond a maximum was due to scattered light obtained when a tungsten lamp was used as the light source rather than the more appropriate hydrogen lamp.

Further exploratory work was carried out at pH 2.0 (0.01 N $HNO_3$) since Beer's law was obeyed at this pH for wavelengths greater than 330 mμ. The studies showed that nitrate ion was responsible for a great deal of the light absorption in the far ultraviolet. The experimental curve for the molar extinction coefficient $\epsilon$ of nitric acid is given in Figure 1 as a function of the wavelength. (The molar extinction coefficient $\epsilon$ is the negative decade logarithm of the transmittance $I/I_0$ for one centimeter light path in a solution containing one mole per liter of absorber.) There is a weak band at 302 mμ and a strong one starting at 250 mμ and extending beyond the range of the instrument. It was found possible to detect $10^{-5}$ M nitric acid with ease at 210 mμ. Considerable difficulty was encountered in adequately cleaning absorption cells that had been used with nitrate solutions because of this very strong absorption.

It was shown that the perchloric acid has no appreciable absorption within the range of the instrument, and therefore all subsequent work was done with perchlorate solutions. It was then shown that the original uranyl nitrate curve was approximately correct for uranyl ion, except for the peak near 225 mμ. The absorption appears to increase indefinitely at shorter wavelengths. This necessitated the use of a much lower peak at 410 mμ for further work. It was also shown that uranyl ion obeys Beer's Law over the range of concentration from 1-40 mg/ml in solutions of pH 2. This is illustrated in Figure 2 which shows the optical density of a number of uranyl solutions of widely differing concentrations and Figure 3 which shows the optical density as a function of concentration for two representative wavelengths. (The optical density D is the negative logarithm to the base 10 of the transmittance; it is equal to the product of the molar extinction coefficient, the molar concentration, and the length of the cell in cm.) Figure 4 gives the absorption spectrum of uranyl ion, as arrived at by averaging all of

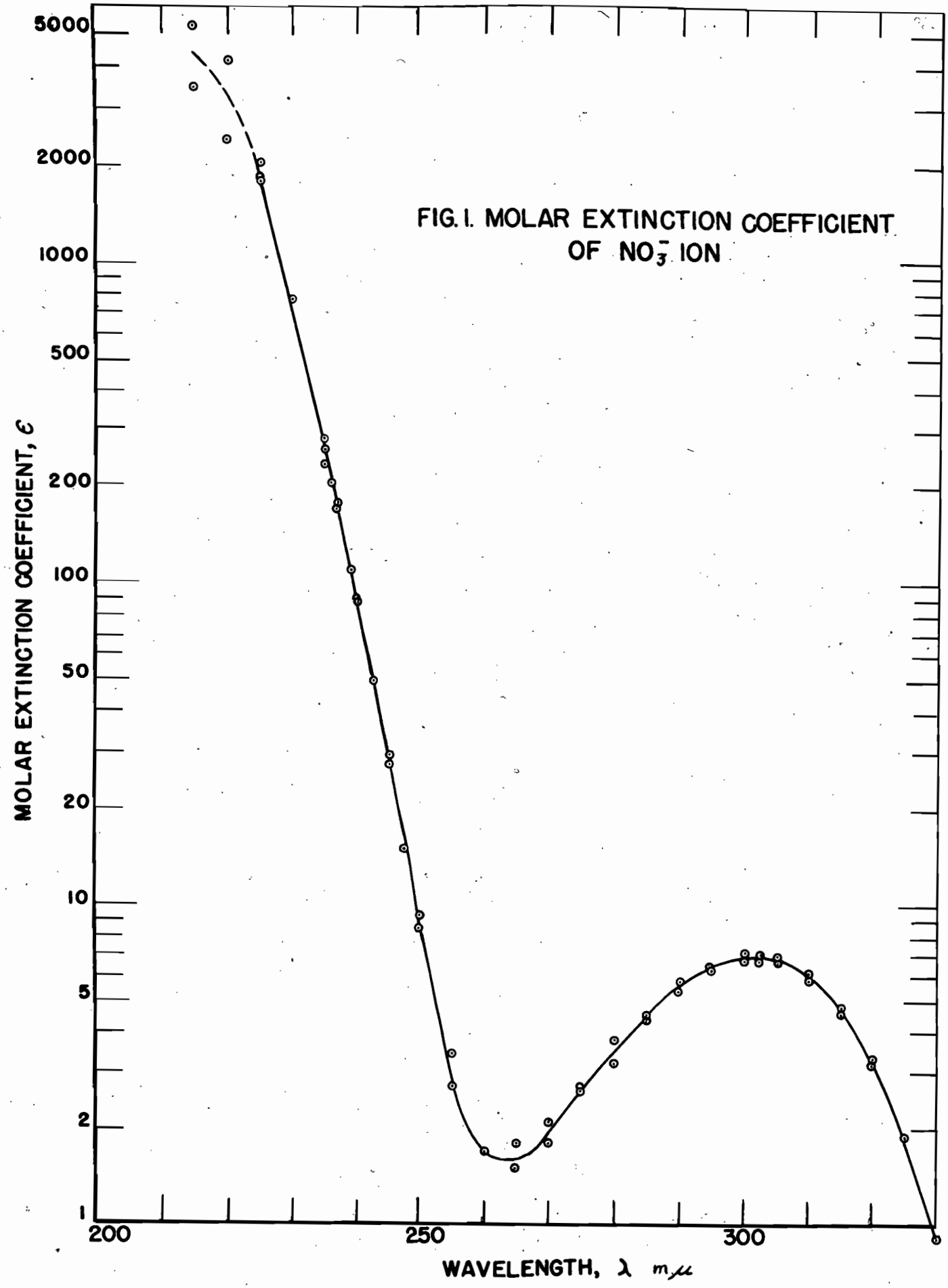


FIG. I. MOLAR EXTINCTION COEFFICIENT OF $NO_3^-$ ION

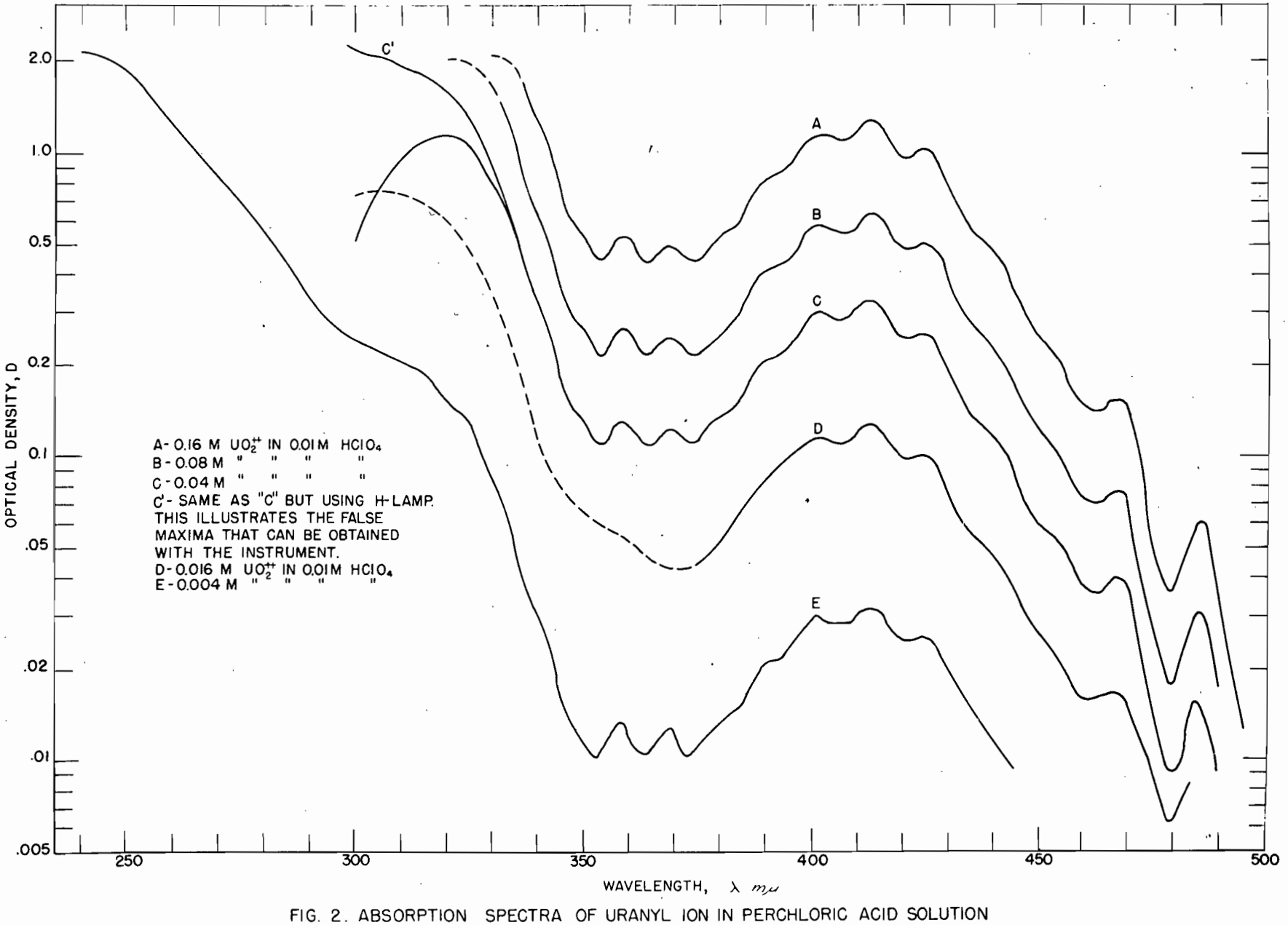


FIG. 2. ABSORPTION SPECTRA OF URANYL ION IN PERCHLORIC ACID SOLUTION

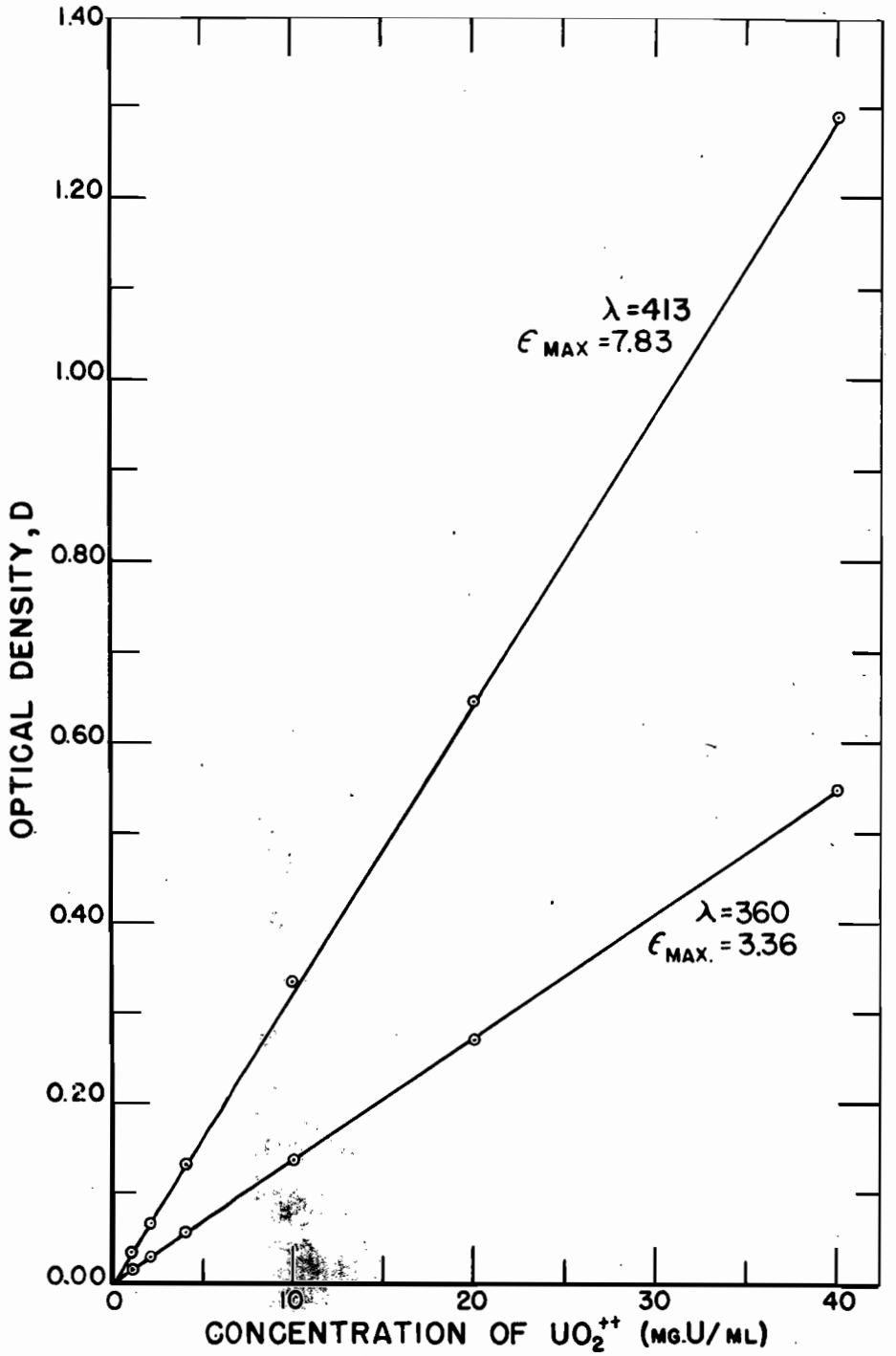


FIG.3. TEST OF BEER'S LAW FOR URANYL ION IN PERCHLORIC ACID SOLUTION

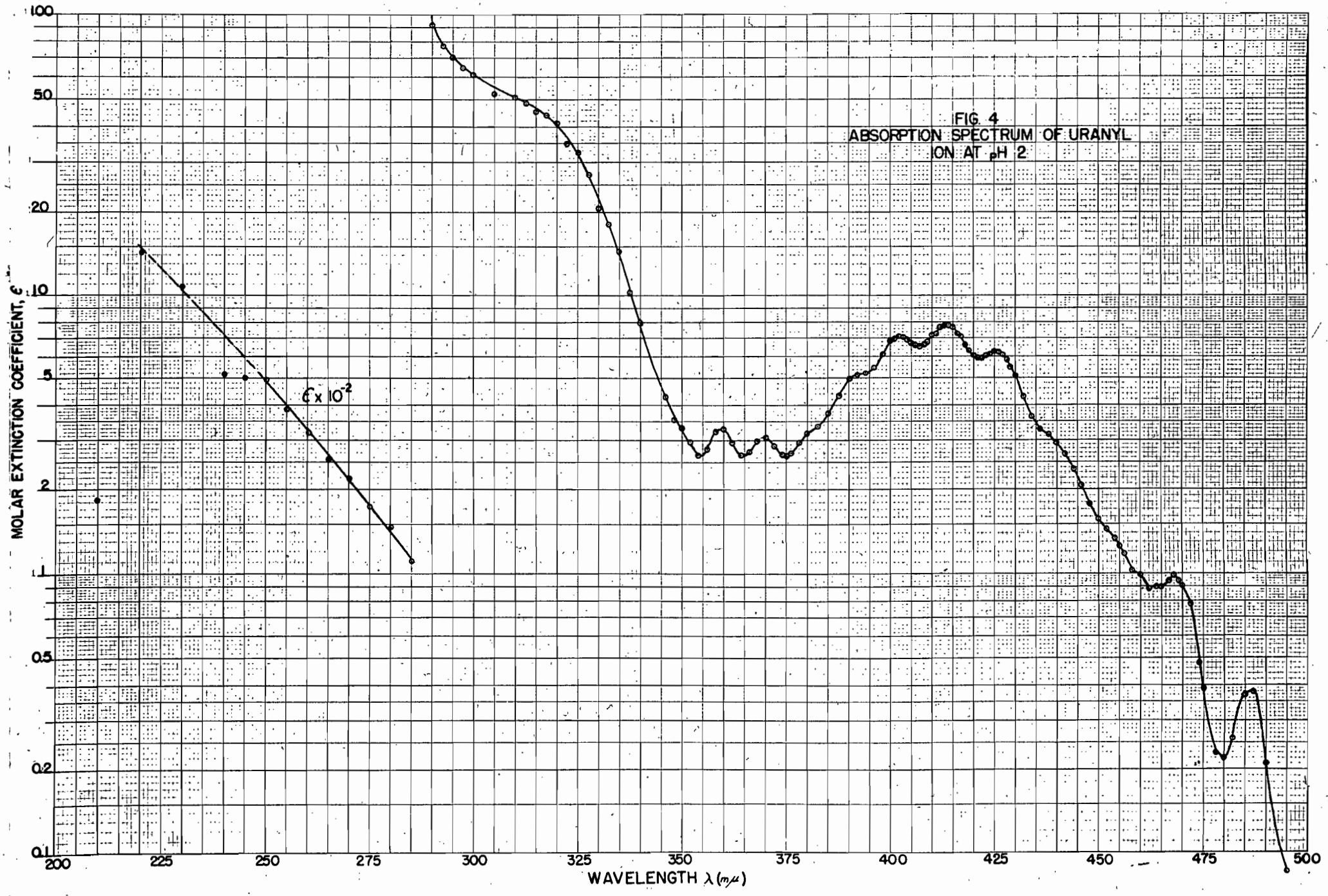
FIG. 4
ABSORPTION SPECTRUM OF URANYL
ION AT pH 2
MOLAR EXTINCTION COEFFICIENT, ε
WAVELENGTH λ (mμ)
ε x 10⁻²
100
50
20
10
5
2
1
0.5
0.2
0.1
200
225
250
275
300
325
350
375
400
425
450
475
500

the molar extinction coefficients obtained from the data used in proving the obedience of Beer's Law. The dotted line below 250 mμ is believed to be the best curve obtainable from the experimental data; the points below this curve are probably due to scattered light in the instrument. The complexity of the curve should be of considerable theoretical interest.

Attempts to extend these studies to solutions in the pH range of 3-5 soon led to many difficulties. At pH 4 it was found that not only is Beer's Law not obeyed, but that duplicate results with solutions which were supposedly identical were difficult to obtain. Upon further checking of these solutions, it was found that the molar extinction coefficient was an extremely sensitive function both of pH and also of uranyl ion concentration. Solutions identical except for a few hundredths difference in pH gave molar extinction coefficient differences of as great as 5 or 10% (Figure 5). At first this was thought to give indication of great promise, since this was a readily observable, very sensitive function both of pH and of uranyl ion concentration. It soon became apparent, however, that the optical measurements were too sensitive, for pH meter inconsistencies* and analytical difficulties were great enough to make it impossible to obtain a consistent set of data. Procurement of a new pH meter and reconditioning of the old one reduced these difficulties somewhat but experimental scattering of the points was still observed.

## Interpretation of the Results

A search of the literature for quantitative data or theory of the hydrolysis of uranyl ion showed that the paper of Best, Taub, and Longsworth[1] is virtually the only contribution in the field. They present two theories of hydrolysis. The first involved a two step hydrolysis:

$$UO_2{\cdot}OH^{+} \rightleftharpoons UO_3 + H^{+} \qquad (1)$$

$$UO_2^{++} + H_2O \rightleftharpoons UO_2{\cdot}OH^{+} + H^{+} \qquad (2)$$

Mass action constants, based on concentrations rather than activities, for these reactions of $K_1 = 4.6 \times 10^{-4}$ and $K_2 = 6.0 \times 10^{-5}$ fit their data satisfactorily for the pH of solutions of $UO_3$ in HCl, but failed

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* The perchlorate concentration in these solutions was 0.01 M. It is possible that some of the difficulty encountered in measuring the pH was due to precipitation of $KClO_4$ in the salt bridge of the calomel electrode.

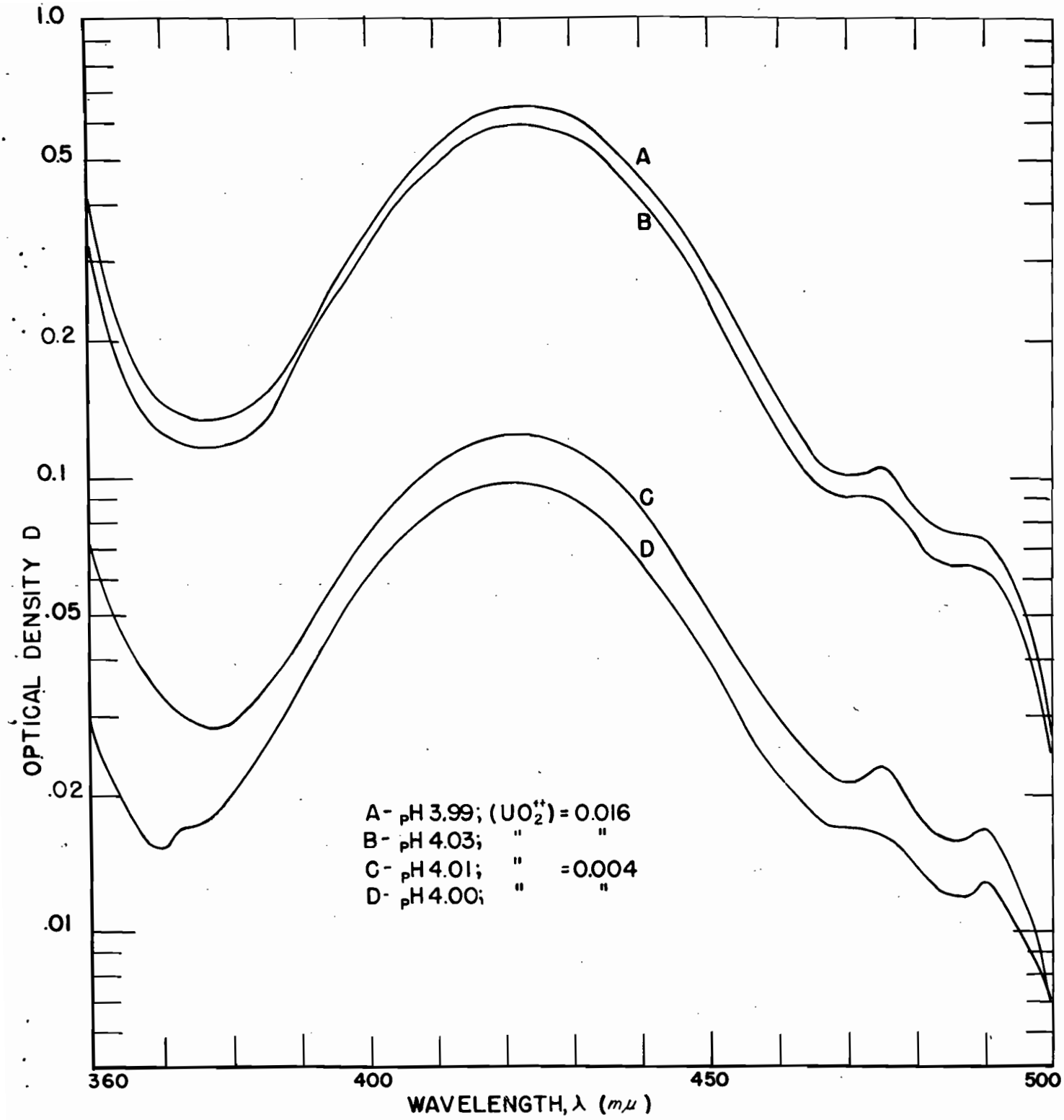


FIG. 5. ABSORPTION SPECTRA OF VERY SIMILAR URANYL SOLUTIONS

completely to fit the data for the pH of uranyl chloride solutions as a function of concentration. They discard this theory therefore in favor of one depending on the dimerization of uranyl ion, as follows:

$$2\ UO_2^{++} + H_2O \equiv UO_3 \cdot UO_2^{++} + 2H^+ \qquad (3)$$

For this equation they give the concentration mass action constant $K' = 1.35 \times 10^{-6}$. It was decided to make a critical study of their data to see how sensitive the titration and hydrolysis curves were to various trial values of K'. Values of the pH as a function of $[UO_3]/[HCl]$ or of $[UO_2Cl_2]$ were calculated for values of K' varying from $1.00 \times 10^{-6}$ to $1.60 \times 10^{-6}$ and the curves were plotted along with their experimental data, in order to study the effect of the constant on the fit to the observations. Since the pH meter measures hydrogen ion activity, it was necessary to convert the readings to concentration. This was accomplished through the use of the activity coefficients estimated by Best, Taub and Longsworth. These studies, shown in Figures 6 and 7, indicate that $K' = 1.35 \times 10^{-6}$ gives the best fit to both sets of data. It will be noted that the calculated curves fail to explain the low pH of the solution wit 0.90 equivalents of $UO_3$ per equivalent of HCl. This discrepancy might be explained by the formation of the ion $U_3O_8^{++}$. Attempts to formulate a quantitative picture including this third constituent were dropped because of mathematical difficulties.

A preliminary attempt to fit the present results to this theory was promising enough to warrant a detailed study. If the ionic species in Equation (3) are the only colored ones present, the observed gross molar extinction coefficient $\epsilon_{obs}$, should be a linear function of the fraction F of the total uranium ion in the dimeric form:

$$\epsilon_{obs} \equiv \epsilon_{UO_2^{++}}(1-F) + \frac{\epsilon_{U_2O_5^{++}}}{2} F \equiv \epsilon_{UO_2^{++}} + \left(\frac{\epsilon_{U_2O_5^{++}}}{2} - \epsilon_{UO_2^{++}}\right) F \qquad (4)$$

The method of calculation of F follows. Let $x \equiv [UO_2^{++}]$, $w \equiv [UO_3 \cdot UO_2^{++}]$, $h \equiv [H^+]$, and then the total uranium concentration $c \equiv x + 2w$. From equation (3):

$$K' \equiv \frac{wh^2}{x^2} = \frac{wh^2}{(c-2w)^2}$$

$$4\ K'w^2 - 4\ K'cw - wh^2 + K'c^2 \equiv 0.$$

$$4\ K'w^2 - (4\ K'c + h^2)\ w + K'c^2 \equiv 0.$$

$$w \equiv \frac{4\ K'c + h^2 \pm h\sqrt{8\ K'c + h^2}}{8K'} \qquad (5)$$

$$F \equiv 2w/c \qquad (6)$$

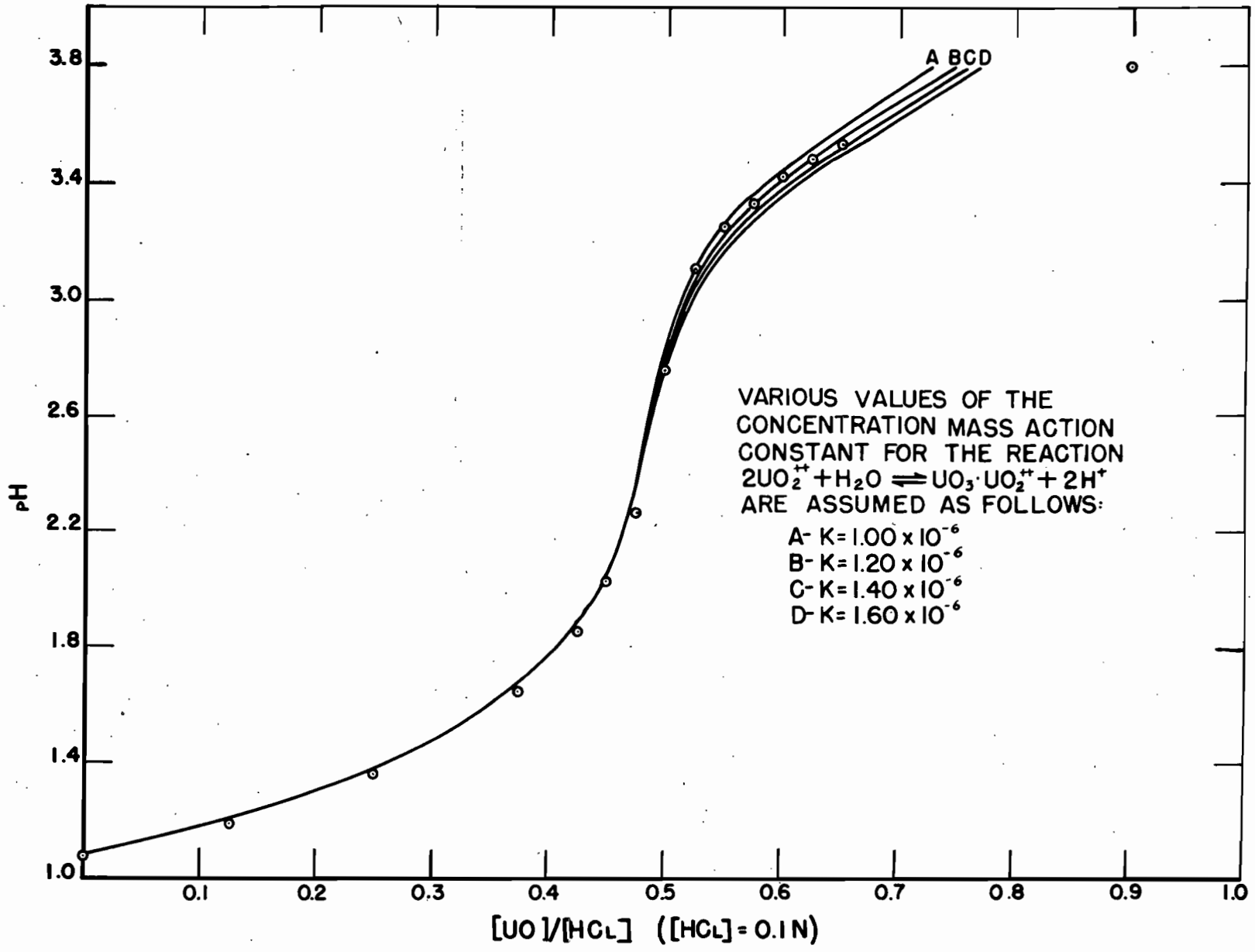


FIG. 6. FIT OF EXPERIMENTAL TITRATION DATA TO THEORETICAL CURVE

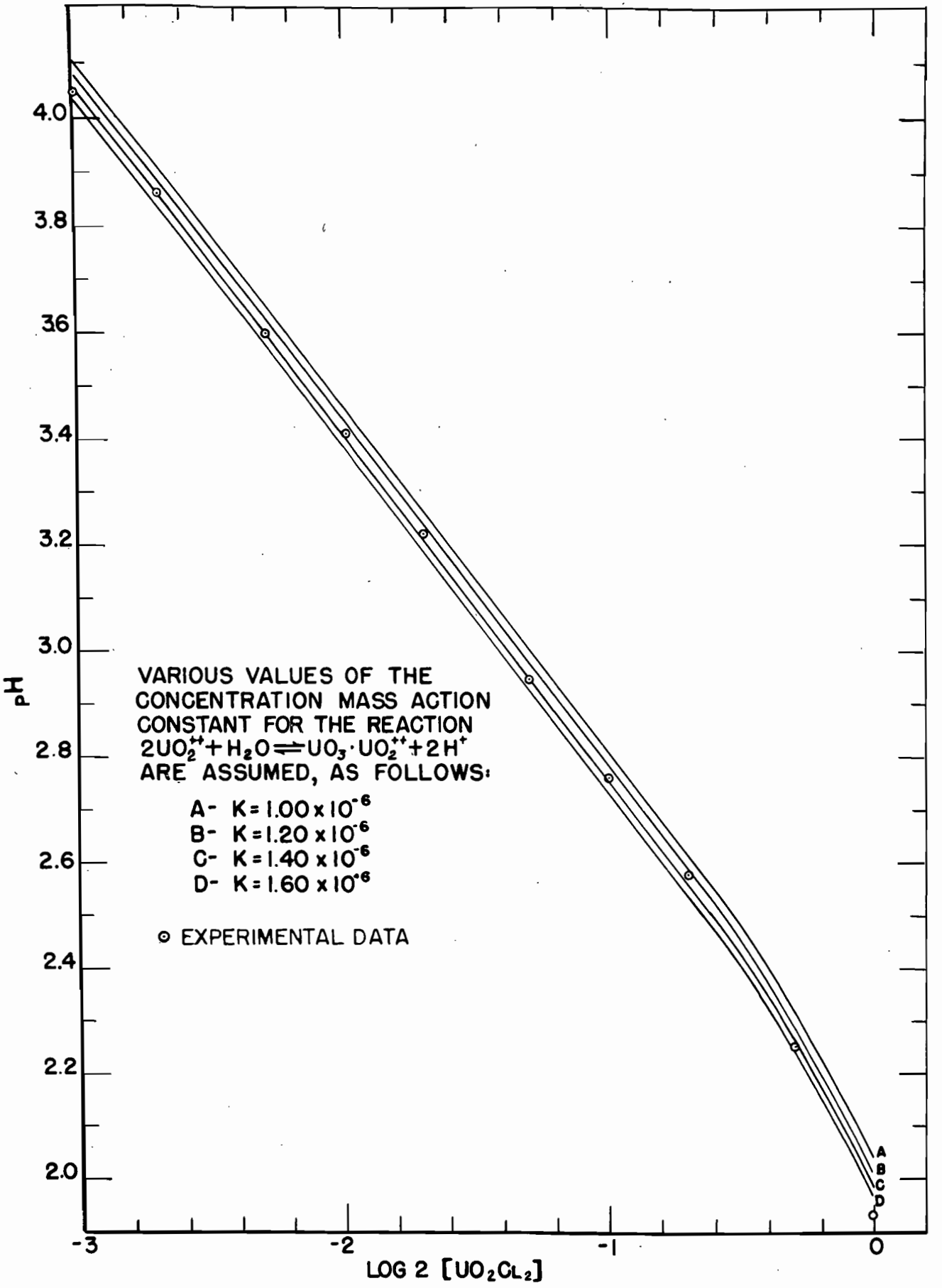


FIG. 7. FIT OF EXPERIMENTAL HYDROLYSIS DATA TO THEORETICAL CURVE

Values of w and F were calculated from the measured pH values and total uranium concentrations, c, for a large number of solutions with pH values from 2 to 4.3 and with $U^{VI}$ concentration from 0.08 to 0.004 M. In Figure 8 there is plotted the observed molar extinction coefficient, $\epsilon_{obs}$, at 420 mμ as a function of this degree of dimerization, F. The deviation from the predicted linear relation (Equation (4)) is greater than can be attributed to experimental error. The curved line is the best that can be drawn through the experimental points; the straight broken line indicates the possible linear behavior up to F ≅ 0.40, where equation (3) has the greatest possibility of representing the reactions in solution. The upsweep beyond this value is probably due to the formation of higher polymers (as for instance $U_3O_8^{++}$) with greater extinction coefficient per U atom than occurs for $U_2O_5^{++}$, which itself must have a greater absorption coefficient per U atom than $UO_2^{++}$ in order to account for the observed facts.

The absorption characteristics of hydrolyzed uranyl solutions show interesting qualitative as well as quantitative changes from the spectrum of unhydrolyzed uranyl solutions. The fine structure in the spectrum of the solution at pH 2 disappears gradually as the degree of hydrolysis increases and the peak originally at 413 mμ broadens and shifts a few millimicrons to longer wavelengths. This is shown graphically in Figure 9, which has several curves showing the absorption spectra of solutions predicted to be hydrolyzed to various degrees.

## REFERENCES

(1) Best, R. J., D. Taub, and L. G. Longsworth; A-380, November 24, 1942.

(2) Goldring, L. S.; CL-CDC-#11, March 1945.

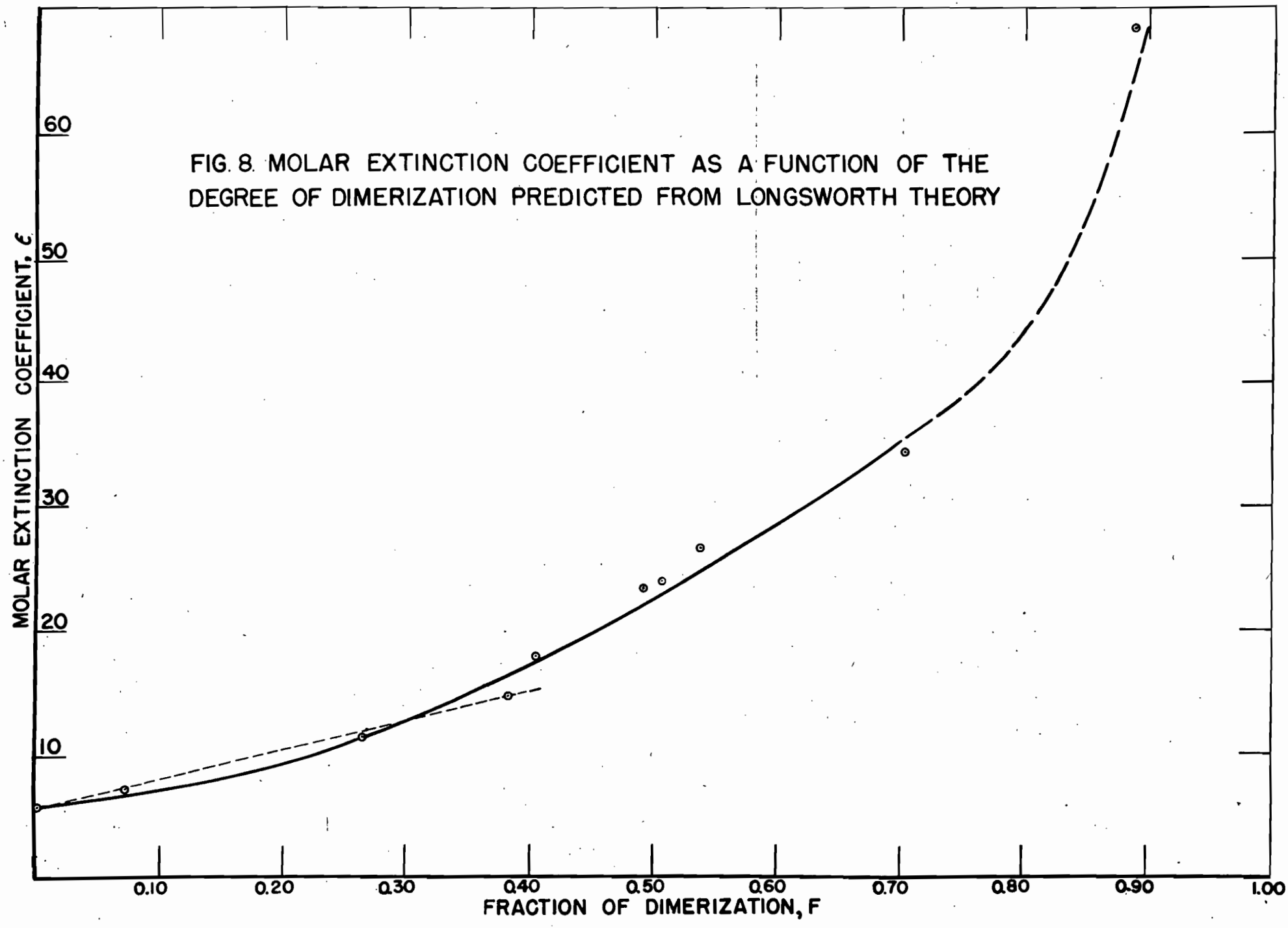


FIG. 8. MOLAR EXTINCTION COEFFICIENT AS A FUNCTION OF THE DEGREE OF DIMERIZATION PREDICTED FROM LONGSWORTH THEORY

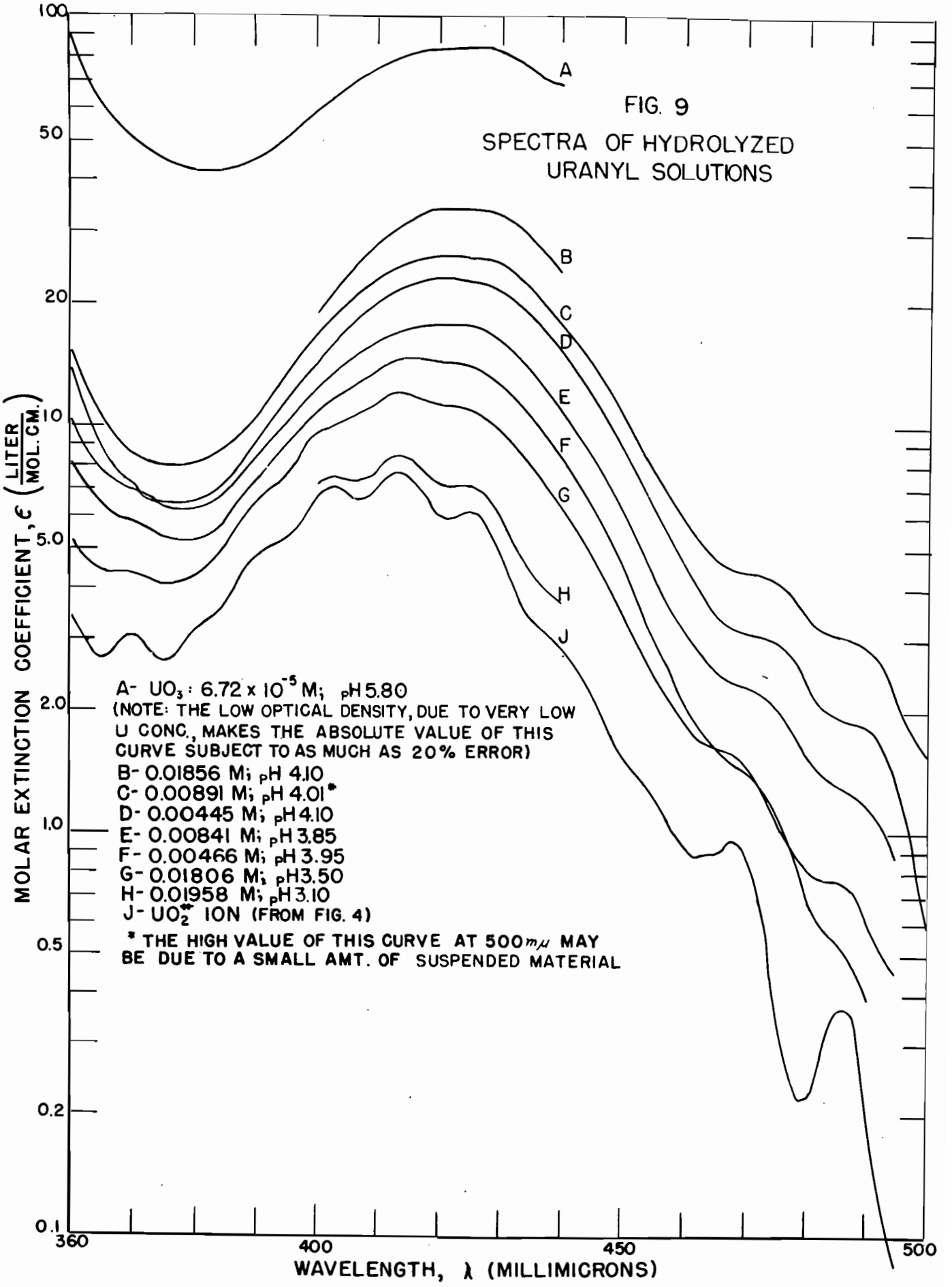
FIG. 9
SPECTRA OF HYDROLYZED URANYL SOLUTIONS
A
B
C
D
E
F
G
H
J
A- $UO_3$: $6.72 \times 10^{-5}$ M; pH 5.80
(NOTE: THE LOW OPTICAL DENSITY, DUE TO VERY LOW U CONC., MAKES THE ABSOLUTE VALUE OF THIS CURVE SUBJECT TO AS MUCH AS 20% ERROR)
B- 0.01856 M; pH 4.10
C- 0.00891 M; pH 4.01*
D- 0.00445 M; pH 4.10
E- 0.00841 M; pH 3.85
F- 0.00466 M; pH 3.95
G- 0.01806 M; pH 3.50
H- 0.01958 M; pH 3.10
J- $UO_2^{++}$ ION (FROM FIG. 4)
* THE HIGH VALUE OF THIS CURVE AT 500 mμ MAY BE DUE TO A SMALL AMT. OF SUSPENDED MATERIAL
MOLAR EXTINCTION COEFFICIENT, ε (LITER / MOL. CM.)
100
50
20
10
5.0
2.0
1.0
0.5
0.2
0.1
360
400
450
500
WAVELENGTH, λ (MILLIMICRONS)

JUN 1946
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