S 58. *Ionic Association in Aqueous Solutions of Uranyl Sulphate and Uranyl Nitrate.*

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Spectrophotometric methods have been used to study ionic association in aqueous solutions of uranyl nitrate and uranyl sulphate. The stoicheiometric association constants for the equilibria $UO_2^{++} + HSO_4^- \rightleftharpoons UO_2SO_4 + H^+$ and $UO_2^{++} + NO_3^- \rightleftharpoons UO_2NO_3^+$ were found to be 5·0 ± 0·34 and 0·21 ± 0·01, respectively. These values were obtained for solutions 2·00M. in hydrogen ion. Results for concentrations of nitrate greater than 3M. could not be interpreted unequivocally. In this region, either small amounts of $UO_2(NO_3)_2$ are formed, or, more probably, the value of the association constant changes slightly with the ionic environment.

The exchange of uranium atoms between U(VI), (UO_2^{++}), and U(IV) is now known to occur at a measurable rate in sulphuric acid solutions (Betts, *Canadian J. Res.*, 1948, *B*, **26**, 702). However, more recent investigations by one of us (R. H. B.), which will be reported elsewhere, have shown that in perchloric acid solutions the exchange reaction proceeds at a markedly slower rate. In view of the generally non-complexing nature of the perchlorate ion, this result points to the formation of complex ions of U(IV) and U(VI) in sulphuric acid, and has led to a study of the differences in ionic configurations of U(IV) and U(VI) in sulphate and perchlorate solutions. The present paper describes the nature of the species present in uranyl sulphate solutions. Complexes of U(VI) with anions other than sulphate, while not directly concerned with the exchange reaction, are of general interest, and accordingly a study of nitrate complexes of U(VI) has been included. Corresponding studies of the complexing of U(IV) in sulphate solutions are still in progress, and will be reported later.

Several references to anion complexes of U(VI) occur in the literature. Kolthoff and Harris (*J. Amer. Chem. Soc.*, 1946, **68**, 1175), on the basis of polarographic investigations, gave a qualitative account of complexing of U(VI) by various anions. In the order of increasing stability of the complex, they listed perchlorate, chloride, sulphate, and oxalate. Sutton (Report 1612, National Research Council, Ottawa, Canada) reported that both sulphate and chloride form complexes with U(VI), while perchlorate does not.

More quantitative information is available concerning the hydrolysis of the uranyl ion : $UO_2^{++} + H_2O \rightleftharpoons UO_2(OH)^+ + H^+$. The hydrolysis constant for the species UO_2^{++} is given as $8{\cdot}1 \times 10^{-5}$ by Kolthoff and Harris (*J. Amer. Chem. Soc.*, 1947, **69**, 446). Sutton (*loc. cit.*) reported substantially the same value, although his formulation of the hydrolysis differs somewhat from that given by Kolthoff and Harris. Sutton also showed that the absorption spectrum of the uranyl ion in perchloric acid does not change until the hydrogen-ion concentration is less than 0·01M.

Spectrophotometric methods have been used in the present investigation. They depend for their usefulness on the fact that, in general, complex and simple ions absorb light to a different extent. Job (*Ann. Chim.*, 1928, **9**, 113) and, more recently, Vosburgh (*J. Amer. Chem. Soc.*, 1941, **63**, 437) have developed a spectrophotometric technique, called the method of continuous variations, which in many cases, leads directly to the formula of the complex ion. Solutions are prepared of constant ionic strength and fixed *total* concentration of cation plus complexing agent. The ratio of the concentrations of cation to complexing agent is varied over a fairly wide range through the series. The optical density of these solutions is then measured at several wave-lengths, and the results compared to the expected values if no interaction takes place between the two components. A plot of this difference, for a given wave-length, against the composition of the solution shows a maximum or a minimum according as the complex absorbs light more or less strongly than either of the components. It can be shown (Vosburgh, *loc. cit.*) that the value of the ratio of the concentration of cation to that of total concentration of cation plus complexing agent, at the point of inflection of this curve, bears a simple relation to the formula of the complex ion.

When the formula of the complex species is known, it is comparatively simple to deduce the value of the corresponding association constant. The method will be illustrated for the complex ion $UO_2NO_3^+$ formed from one ion of UO_2^{++} and one ion of NO_3^-, since this is the type of complex we deal with in this paper (see below).

For a given wave-length and in the absence of complexing agents (*e.g.*, in perchloric acid solutions), the optical density, D_i, of a solution of U(VI) is given by the usual expression

$$D_i = l.E_U(i)[U(VI)] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which l is the length of the cell in cm., $E_U(i)$ is the value of the extinction coefficient of U(VI) for the given wave-length, and [U(VI)] is the molar concentration of U(VI). The optical density is defined by the relation $D = \log I_0/I$, in which I is the intensity of light transmitted by the uranium solution, and I_0 that of the same solution in the absence of uranium. Since absorption cells of 1-cm. path have been used in this work, the factor l will be omitted.

In the presence of NO_3^-, some of the species $UO_2NO_3^+$ is formed, and the equilibrium expression is

$$UO_2^{++} + NO_3^- \rightleftharpoons UO_2NO_3^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The optical density of such a solution is given by

$$D_i = E_U(i)[UO_2^{++}] + E_C(i)[UO_2NO_3^+] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

in which the subscripts U and C refer to UO_2^{++} and $UO_2NO_3^+$, respectively. The association constant for the equilibrium, in terms of molar concentrations, is

$$[UO_2NO_3^+]/[UO_2^{++}][NO_3^-] = K \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

(Since all experiments in a comparable series in this work were made at nominally constant ionic strength, the activity-coefficient factors in all equilibria have been assumed to remain constant. Accordingly, association constants will be defined in terms of molar concentrations. The consequences of this assumption are discussed more fully in connection with certain of the experimental results.)

To determine K, we proceed as follows: Let the concentration of $UO_2NO_3^+$ be a_1, in a solution initially c_1M. in nitrate and u_1M. in U(VI). Then the association constant is given by

$$a_1/(u_1 - a_1)(c_1 - a_1) = K \quad (5)$$

If c_1 and a_1 are chosen so that $c_1 \gg u_1$, then $c_1 \gg a_1$, and as a good approximation

$$a_1/(u_1 - a_1) = c_1K \quad (6)$$

Equation (6) may be solved for a_1, leading to

$$a_1 = Kc_1u_1/(1 + Kc_1) \quad (7)$$

The optical density D_1 for a fixed wave-length λ_1 is given by

$$D_1 = E_U(u_1 - a_1) + E_Ca_1 \quad (8)$$

By substituting for a_1 in (8) from (7), equation (8) leads to

$$E_C = (D_1 + c_1KD_1 - E_Uu_1)/c_1Ku_1 \quad (9)$$

For a second solution containing initially c_2M-nitrate and u_2M-U(VI), an expression similar to (9) may be obtained for E_C in terms of K, D_2, c_2 and u_2. Provided that optical densities for the same wave-lengths are used, these two expressions for E_C may be equated and solved for K in terms of measurable quantities:

$$K = \frac{c_2u_2D_1 - c_1u_1D_2 - E_Uu_1u_2[c_2 - c_1]}{c_1c_2[u_1D_2 - u_2D_1]} \quad (10)$$

The value of the association constant may be calculated for all wave-lengths for which D_1, D_2, and E_U are known. Errors introduced in the original approximation in equation (6) may now be reduced, if required, by a second approximation. We found, in fact, that a second approximation was unnecessary.

Values for $E_C(i)$ may be obtained from a knowledge of K and $E_U(i)$ by use of equations (3) and (4).

The presence of other possible complexes at higher concentrations of complexing agent may be observed by comparing the measured optical densities with those calculated from a knowledge of K, $E_U(i)$, and $E_C(i)$. Any discrepancies in such comparisons will point to the formation of new species in solution, provided, of course, that the correct values of K and $E_C(i)$ are obtained for the first complex.

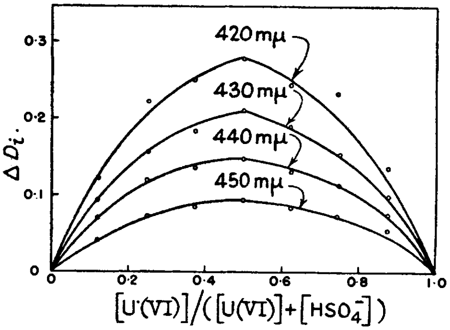
Experimental Results and Discussion.—A standard solution of uranyl perchlorate in 2·00M-perchloric acid was prepared by dissolving pure uranium trioxide in the required amount of the chloride-free acid. Sodium perchlorate solutions were prepared from sodium hydroxide and perchloric acid. Standard solutions of sulphuric acid and sodium nitrate were prepared from reagent-grade materials. Solutions required in the experiments were prepared by weight from these stock solutions. All experiments in a comparable series were made at the same apparent ionic strength, by use of sodium perchlorate.

A Beckman Model DU Spectrophotometer was used in this investigation. It was equipped with a water-cooled face plate, mounted as an integral part of the cell compartment, through which water at 25·0° was circulated. One-cm. Corex cells were used. Cell corrections were determined at frequent intervals, and corrections made where necessary.

(A) *Complexes with Perchlorate.*—Extinction coefficients for U(VI) in perchloric acid–sodium perchlorate mixtures were determined over the region 340—500 mμ, at 2-mμ intervals. The concentration of U(VI) was varied from 0·02 to 0·5M., and the perchlorate concentration from 2·0 to 6·0M. The hydrogen-ion concentration was maintained at 2·00M. No significant variations in the extinction coefficients were found over this range of concentrations for any wave-length. A typical plot of E_U against λ is given in Fig. 2 (lower curve). This result indicates that perchlorate does not form any complexes with U(VI), and confirms Sutton's observations (*loc. cit.*) made over a narrower range of concentrations.

(B) *Complexes with Sulphate.*—Solutions were prepared, 2·00M. in hydrogen ion, with a constant ionic strength of 2·65. [Sulphuric acid has been treated as a monobasic acid for purposes of calculating the hydrogen-ion concentration or the ionic strength. This of course is not strictly correct, but represents a good approximation in view of the value 0·010 at 25° reported for the second dissociation constant of sulphuric acid (Harned and Owen, "Physical Chemistry of Electrolytic Solutions," Reinhold, New York, 1943, p. 430).] The solutions contained varying ratios of U(VI) to bisulphate, but the total concentration of these species was kept constant at 0·240M. The optical densities of these solutions were measured over the region 420—450 mμ. The difference ΔD_i between the observed optical densities and those calculated for no interaction (on the basis of results in Section A above) were plotted against the value of the mole ratio $[U(VI)]/([(U(VI)] + [HSO_4^-])$. The results for representative wave-lengths are given in Fig. 1. A maximum was found for each wave-length at a mole ratio of 0·5. This value indicates that a complex of U(VI) containing either one sulphate or one bisulphate is formed in solution (Vosburgh, *loc. cit.*).

FIG. 1.



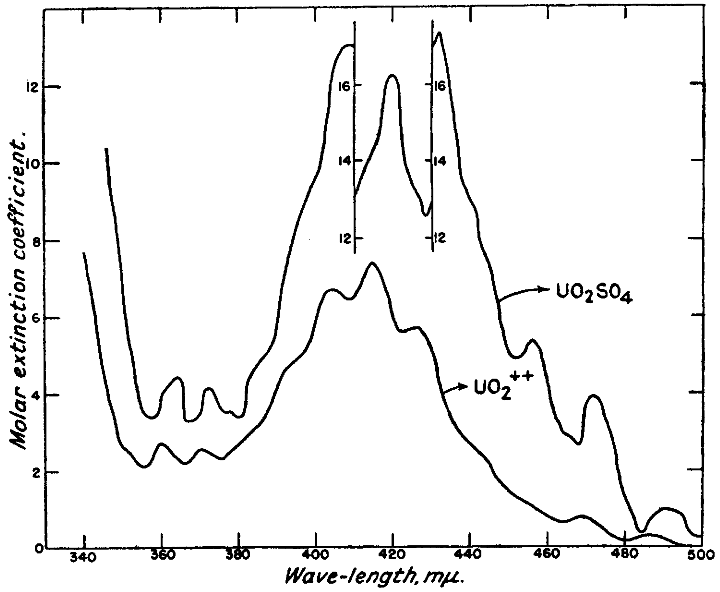
To distinguish between these possibilities, we may consider the effect of changes in the hydrogen-ion concentration on the following equilibria :

$$UO_2^{++} + HSO_4^- \rightleftharpoons UO_2HSO_4^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

and

$$UO_2^{++} + HSO_4^- \rightleftharpoons UO_2SO_4 + H^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

FIG. 2.



If the complex is $UO_2HSO_4^+$, its concentration will be virtually independent of acidity for a fixed concentration of sulphuric acid. If, on the other hand, the complex is UO_2SO_4, its concentration will increase as the acidity is decreased. Fig. 3 gives the relevant experimental results. The values of ΔD_i, which give a measure of the concentration of complex, increase as the acidity is decreased. Clearly then, the complex species is UO_2SO_4, and the association constant is given by

$$[UO_2SO_4][H^+]/[UO_2^{++}][HSO_4^-] = K_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

Since in this work, the acidity was fixed at 2·00M., it is convenient to define a new equilibrium constant K_2, such that $K_1 = K_2[H^+]$, leading to

$$[UO_2SO_4]/[UO_2^{++}][HSO_4^-] = K_2 \qquad (14)$$

The value of the association K_2 was now determined, using two solutions 0·175 and 0·350M. in bisulphate. The acidity was fixed at 2·00M. in each, the U(VI) concentration at 0·020M., and the ionic strength at 3·48. Values of K_2 were calculated for 16 wave-lengths between 420 mμ and 450 mμ, using equation (10). This led to an average value of 2·50 ± 0·17 for K_2.

FIG. 3.

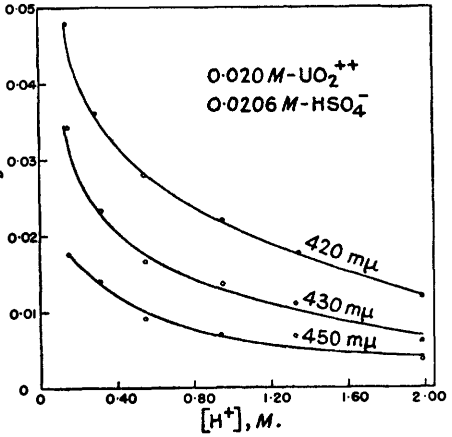
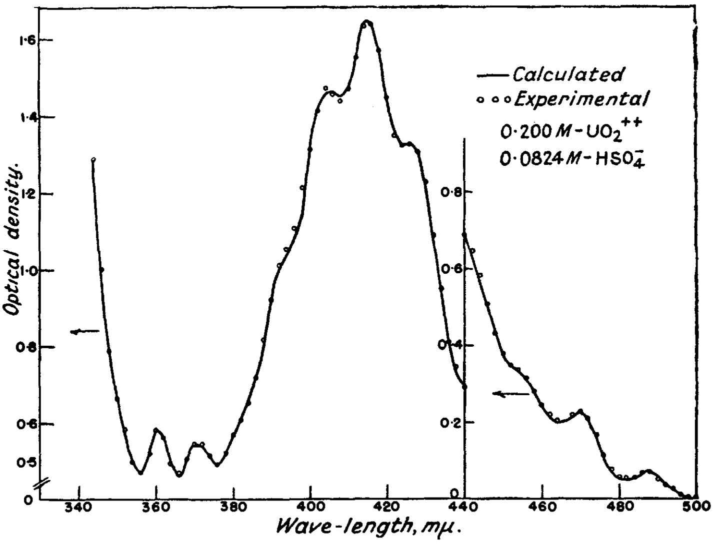


FIG. 4.



Extinction coefficients for the species UO_2SO_4 were obtained from 340 to 500 mμ. The optical density of a solution 0·100M. in U(VI), 0·0824M. in bisulphate, and ionic strength 3·48 was determined over this region, and $E_C(i)$ calculated from a knowledge of K_2 and $E_U(i)$ by using the appropriate form of equations (3) and (14). The result is given in Fig. 2.

To check the validity of the foregoing treatment, two solutions were prepared with the same ionic strength and acidity as that used previously, but with different bisulphate and U(VI) concentrations. The optical densities of these solutions were compared with the values to be expected from a knowledge of $E_U(i)$, $E_C(i)$, and K_2. The calculated and observed values for these solutions, together with other data, are given in Figs. 4 and 5.

In another series, the concentration of bisulphate was increased in steps up to 1·225M., with the concentration of U(VI) fixed at 0·020M. The observed and calculated optical densities for several wave-lengths are given as a function of the bisulphate concentration in Fig. 6. This result, together with those shown in Figs. 4 and 5, lends support to the correctness of the values of $E_C(i)$ and K_2. Also, we conclude that no appreciable concentration of complexes other than UO_2SO_4 exists in the range 0—1·22M-bisulphate.

FIG. 5.

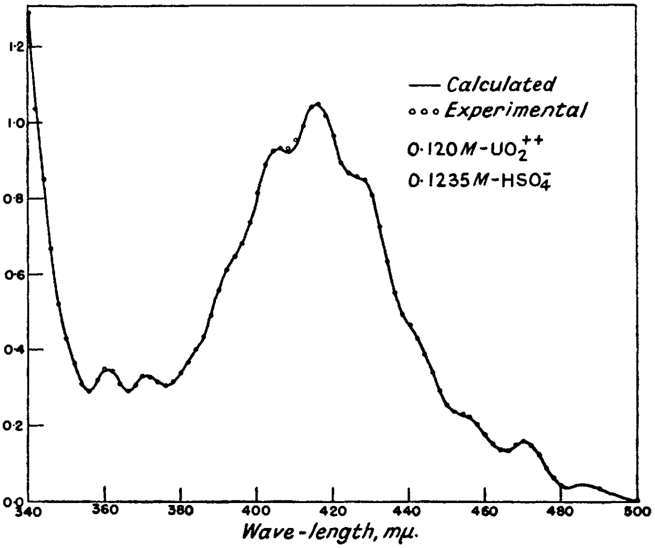
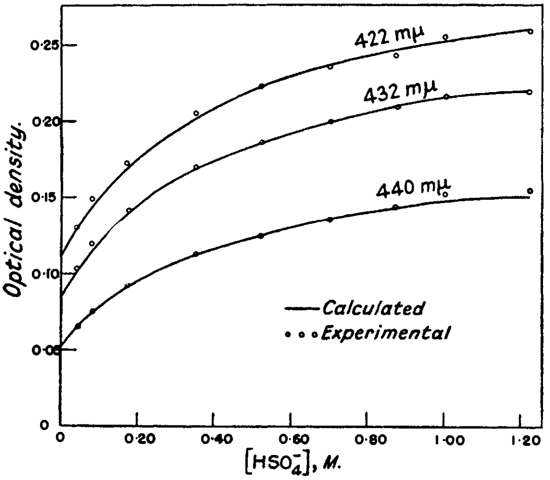


FIG. 6.

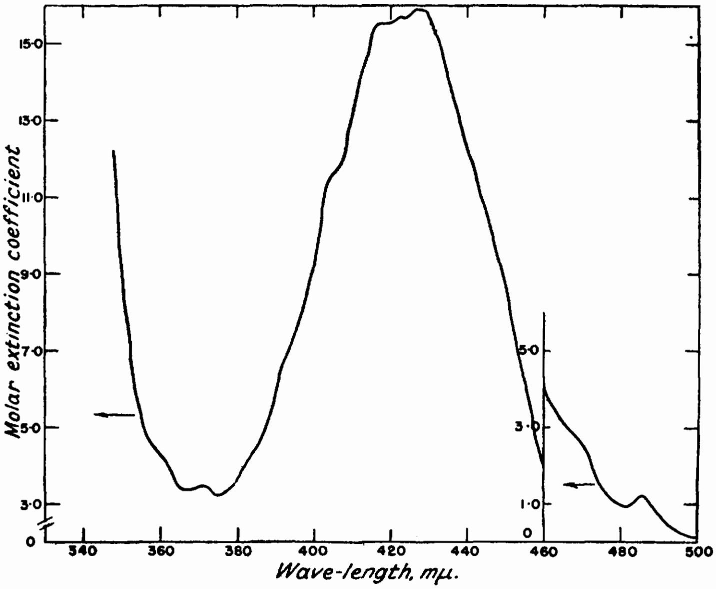


(C) *Complexes with Nitrate.*—Preliminary experiments showed that nitrate formed a weak complex with U(VI). The method of continuous variations (Vosburgh, *loc. cit.*) was then used to determine the formula of the complex species. Solutions were prepared 2·00M. in hydrogen ion, and the total concentration of U(VI) plus nitrate was fixed at 0·50M. The differences between the observed optical densities and those calculated on the basis of no complexing, showed maxima for every wave-length examined at a mole ratio $[U(VI)]/([U(VI)] + [NO_3^-])$ of 0·5. This result indicates that the complex species is $UO_2NO_3^+$. The association constant is given by

$$[UO_2NO_3^+]/[UO_2^{++}][NO_3^-] = K_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

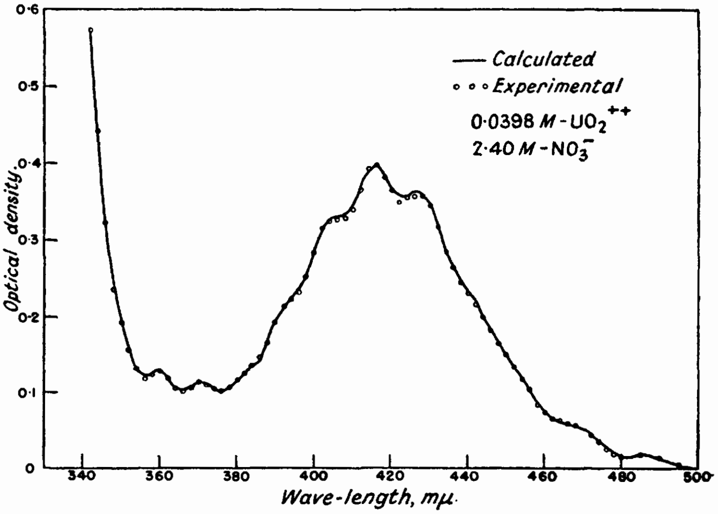
The value of K_3 was now determined in the manner described earlier, two solutions being used, *viz.*, (i) 1·28M-nitrate, 0·0605M-U(VI), and (ii) 2·56M-nitrate, 0·0609M-U(VI). The acidity was fixed at 2·00M. as before, and the ionic strength at 5·38. The average value of K_3 from 14 wave-lengths was found to be 0·21 ± 0·01. Extinction coefficients for the species $UO_2(NO_3)^+$ are given in Fig. 7. Figs. 8 and 9 show the comparison between the observed and the calculated optical densities for two new solutions of U(VI) and nitrate. This agreement substantiates our values of $E_C(i)$ and K_3.

FIG. 7.



Absorption spectrum of $UO_2NO_3^+$.

FIG. 8.



A search was now made for other complexes at increased nitrate concentrations, for which it was necessary to change the ionic strength from 5·38 to 7·05. The association constant K_3 was re-determined at this ionic strength, using a solution 0·040M. in U(VI) and 0·500M. in nitrate. K_3 was calculated from a knowledge of D_i, $E_U(i)$, and $E_O(i)$, by using equations (3) and (4), together with the additional relation that

$$[UO_2^{++}] = [UO_2^{++}]_0 - [UO_2NO_3^{+}] \qquad (16)$$

[The subscript in this equation characterises the total concentration of U(VI), including that part bound in the complex.] These calculations were made for 15 wave-lengths, and gave an average value for K_3 of 0·270 ± 0·007.

FIG. 9.

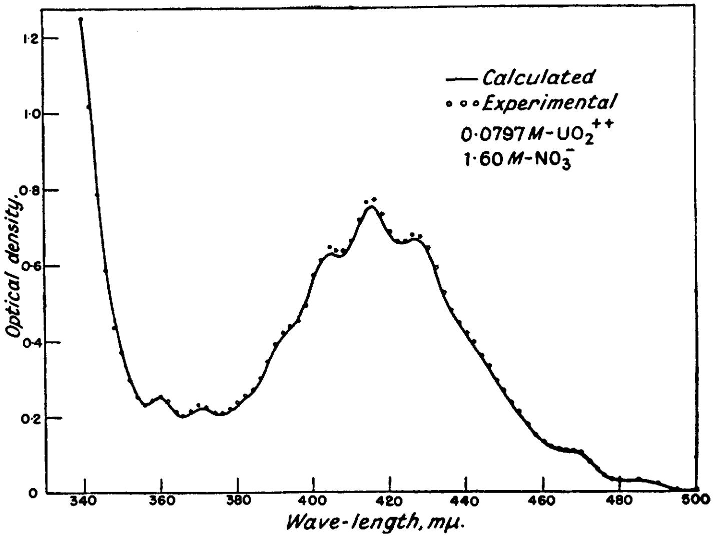
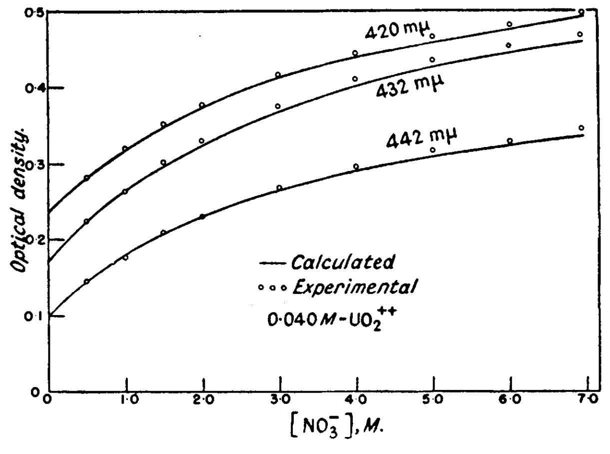


FIG. 10.



The concentration of nitrate was then increased in steps up to 6·95M., nitric acid and sodium nitrate being used. The hydrogen-ion concentration remained at 2·00M., and the ionic strength at 7·05. The observed optical densities for several wave-lengths are compared with those calculated on the basis of $K_3 = 0·27$ in Fig. 10.

At higher concentrations of nitrate, the experimental values of the optical density, for every wave-length, are always slightly higher than those calculated. Although any one deviation in such comparisons can be explained by a relatively small experimental error (3—5%), it is unlikely that such a view will account for the small but systematic differences shown in Fig. 10. Either of two explanations may be suggested. First, small amounts of a more strongly coloured species, *e.g.*, $UO_2(NO_3)_2$, may be present in solution at higher concentrations of nitrate. Secondly, an association " constant " which changes in value from 0·28 to 0·31 between

1·00M- and 6·95M-nitrate would account quite satisfactorily for the results in Fig. 10, without the necessity of considering the species $UO_2(NO_3)_2$ at all. The latter explanation is, in our view, the more reasonable one, since K_3 depends on the activity coefficients of UO_2^{++}, $UO_2NO_3^+$, and NO_3^-. Small differences in the values of these coefficients over this region are to be expected when the anionic contribution to the ionic strength is changed from entirely perchlorate at 0·0M-NO_3^-, to entirely nitrate at 6·95M-NO_3^-. In any case, much larger deviations between the experimental and calculated optical densities would have to be obtained before any reliable quantitative formulation of the phenomena could be made.

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