elemental iridium formed by decomposition of the pentammine at temperatures not greater than 110° catalyzed the hydrogenation of allyl alcohol at the rate shown in Fig. 1. In these experiments, the hydrogenation of 14.6 millimoles of allyl alcohol in 10 ml. of ethanol was catalyzed by 93 mg. of iridium at 30°, a hydrogen pressure of 2 atm., and an agitation rate of 930 r.p.m. By a modification of the method of Brunauer, Emmett and Teller[11] the surface area of the iridium catalyst was found to be 36 $m.^2$/g.

The Action of Potassium Amide upon Bromopentammineiridium(III) Bromide.—In a typical experiment, 1.13 g. of the bromide dissolved and suspended in 20 ml. of liquid ammonia at −33.5° was treated with the potassium amide equivalent to 0.26 g. of potassium in 35 ml. of liquid ammonia. The reaction was rapid and proceeded without liberation of insoluble gases. The pale yellow solution was removed and the dull yellow solid product was washed 6 times with 20-ml. portions of ammonia. Analysis of the combined supernatant solution and washings gave the following results: Ir, 19 mg.; Br, 0.48 g. (calcd. 0.52 g.).

Anal. Calcd. for $Ir(NH_2)_3 \cdot NH_3$: Ir, 74.9. Found: Ir, 74.6.

This product, which failed to give a satisfactory X-ray diffraction pattern, reacts upon exposure to the atmosphere, reacts with water, and is soluble in hot concentrated nitric acid.

A 0.140-g. sample of the solid reaction product was transferred without exposure to the atmosphere to a Pyrex bulb which was then attached to a Toepler pump and evacuated at room temperature; the bulb was then heated slowly by means of an electric furnace. At 115–120° the yellow solid decomposed to form gaseous ammonia and nitrogen, and a black solid. The temperature was increased to 350° and held at this temperature until gas evolution was complete. The weight loss attributable to gas evolution amounted to 0.035 g. or 25.0% of the sample. The weight of the black solid was 0.1053 g. as compared with 0.1049 g. calculated on the assumption that the black solid is elemental iridium; an X-ray diffraction pattern showed only the lines characteristic of iridium.

In independent experiments, iridium(III) amide prepared as described above, was titrated with potassium amide solution. Addition of exactly three moles of KNH_2/mole of $Ir(NH_2)_3$ resulted in complete dissolution of the precipitate and the formation of an intensely brown colored solution.

AUSTIN, TEXAS

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[11] H. E. Ries, R. A. Van Nordstrand and W. E. Kreger, THIS JOURNAL, **69**, 35 (1947).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

A Spectrophotometric Investigation of the Equilibria Existing in Acidic Solutions of Chromium(VI)[1-3]

BY JAMES YING-PEH TONG AND EDWARD L. KING

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Acidic solutions of chromium(VI) are observed to exhibit significant deviations from Beer's law. Measurements of the optical density of chromium(VI) solutions at the wave lengths 370, 380, 390 and 400 mμ enable one to determine the values of the equilibrium quotients for the reactions: $2HCrO_4^- \rightleftharpoons Cr_2O_7^{=} + H_2O$; $H_2CrO_4 \rightleftharpoons H^+ + HCrO_4^-$; $HCr_2O_7^- \rightleftharpoons H^+ + Cr_2O_7^{=}$. At 25° in perchloric acid–lithium perchlorate media of unit ionic strength, the values of the equilibrium quotients for these reactions are $K_d = 98$, $K_{11} = 1.21$ and $K_{22} = 0.85$, respectively. The values of the dimerization quotient, K_d, have been determined as a function of the ionic strength; an extrapolation to zero ionic strength yields the value $K_d^0 = 35.5$.

The equilibria existing in aqueous acidic solutions of chromium(VI) have been studied by a number of investigators.[4] The glass electrode study of the acidity of chromium(VI) solutions by Neuss and Rieman[4] has given the values 3.20×10^{-7} and 43 for the equilibrium constants of the two reactions

$$HCrO_4^- \rightleftharpoons H^+ + CrO_4^{=} \qquad (1)$$

$$2HCrO_4^- \rightleftharpoons Cr_2O_7^{=} + H_2O \qquad (2)$$

In the present work, a spectrophotometric investigation, attention has been confined to solutions in which the hydrogen ion concentration is greater than approximately 10^{-3} *M*. In such media, $CrO_4^{=}$ is not an important species. The relative importance of the species $HCrO_4^-$ and $Cr_2O_7^{=}$ depends upon the total concentration of chromium(VI), and, therefore, at wave lengths where the extinction coefficients of $HCrO_4^-$ and $Cr_2O_7^{=}$ (calculated on the gram-atom/liter concentration basis) are not equal, Beer's law is not obeyed by acidic chromium(VI) solutions.[5] The wave length region in which spectral data provided the most accurate information regarding dimerization was chosen after examining light absorption data obtained over a wide range of wave lengths. Such data obtained at 25°, which are presented in Fig. 1, suggest that the deviations from Beer's law in the region of 400 mμ are of a large enough magnitude to elucidate the dimerization equilibrium.

In order to account for the observed spectral changes with changes of the concentration of chromium(VI) and hydrogen ion, it is necessary to assume that the species $Cr_2O_7^{=}$, $HCr_2O_7^-$, $HCrO_4^-$ and H_2CrO_4 exist in the concentration ranges which have been studied: 10^{-3} to 1.0 *M* hydrogen ion and 4×10^{-5} to 0.013 gram-atom of chromium(VI) per liter. (The upper limit of the chromium(VI) concentration was determined by the maximum value of the optical density which could be determined. While higher concentrations of chromium(VI) would favor the formation of dimeric species, and therefore might be desirable from the point of view of establishing the value of the equilibrium quotient for reaction 2, possible adverse effects would also be introduced. These are the possibility of higher polychromates being present in more concentrated solutions and the uncertainty in the medium effect caused by the presence of ions of multiple charge at appreciable concentrations.)

The various symbols and definitions which are used in this paper are presented in Table I. In the

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(1) This work has been supported in part by the United States Atomic Energy Commission.

(2) Presented at the 124th Meeting of the American Chemical Society, Chicago, Illinois, September, 1953.

(3) From the Ph.D. thesis of James Y.-P. Tong, University of Wisconsin, 1953.

(4) J. D. Neuss and W. Rieman, THIS JOURNAL, **56**, 2238 (1934); references to earlier work are presented in this paper.

(5) The failure of acidic solutions of chromium(VI) to obey Beer's law also has been observed by J. A. Campbell and R. A. Howald, unpublished work.

evaluation of the several equilibrium quotients, one compares the apparent extinction coefficient values for solutions of various composition. It is desirable that *medium effects* associated with these composition changes be kept as small as possible. It is not sufficient to maintain the ionic strength at a constant value, for it is observed that while the activity coefficient of hydrochloric acid is very nearly constant in lithium chloride–hydrochloric acid mixtures of constant ionic strength, it is far from constant in potassium chloride–hydrochloric acid mixtures of constant ionic strength.[6] These observations and the equation developed by Glueckauf[7] suggest that the activity coefficients of ionic species in lithium perchlorate–perchloric acid solutions are reasonably constant. In a spectrophotometric study such as this, it is necessary, in addition, to assume that the composition changes do not alter the values of the extinction coefficients of the several species. Since data will be presented which indicate that the values of the extinction coefficients do not vary appreciably with varying ionic strength, it seems reasonable to assume that they are constant in media of varying composition but constant ionic strength.

TABLE I

SYMBOLS AND DEFINITIONS[a]

$K_{11} = \frac{(H^+)(HCrO_4^-)}{(H_2CrO_4)}$ $K_{22} = \frac{(H^+)(Cr_2O_7^=)}{(HCr_2O_7^-)}$.

$K_d = \frac{(Cr_2O_7^=)}{(HCrO_4^-)^2}$ $K' = \frac{(\text{total dimers})}{(\text{total monomers})^2}$

C = total concn. of chromium(VI) in gram-atoms per l.
y = fraction of chromium(VI) atoms in dimeric forms
$F(y) = y/(1 - y)^2$
$D = \log_{10}(I_0/I)$
l = absorption cell length in cm.
$\epsilon = D_{\text{obs.}}/Cl$, apparent extinction coefficient
$\bar{\epsilon}_1$ = apparent extinction coefficient of monomeric species
$\bar{\epsilon}_2$ = apparent extinction coefficient of dimeric species
ϵ_{12} = extinction coefficient of H_2CrO_4
ϵ_{11} = extinction coefficient of $HCrO_4^-$
ϵ_{21} = extinction coefficient of $HCr_2O_7^-$
ϵ_{20} = extinction coefficient of $Cr_2O_7^=$
$\Gamma/2$ = ionic strength on the molar concentration scale

[a] A formula enclosed by parentheses stands for the molar concentration of that substance. All extinction coefficients are calculated on a gram-atom per liter concentration scale basis.

Experimental

Reagents.—All solutions were prepared using doubly-distilled water. The second distillation was from an alkaline permanganate solution using a Barnstead still.

Reagent grade perchloric acid (Baker or Mallinckrodt), potassium dichromate (Mallinckrodt) and sodium chromate (Mallinckrodt) were used without further purification. Lithium perchlorate (G. F. Smith) was purified by recrystallization from water two or three times. A solution of sodium perchlorate was prepared by the addition of perchloric aci dto reagent grade sodium carbonate (Mallinckrodt).

The perchloric acid was standardized with mercuric oxide or a sodium hydroxide solution which had been standardized against potassium acid phthalate. Dried reagent grade potassium dichromate was used as a primary standard. The concentration of sodium chromate stock solutions was determined iodometrically using a sodium thiosulfate solution which had been standardized against potassium dichromate. The concentration of lithium perchlorate stock solutions was determined by conversion to the sulfate and weighing as such. The concentration of the sodium perchlorate solution was determined by evaporation of a measured volume, drying the residue at 120° and weighing.

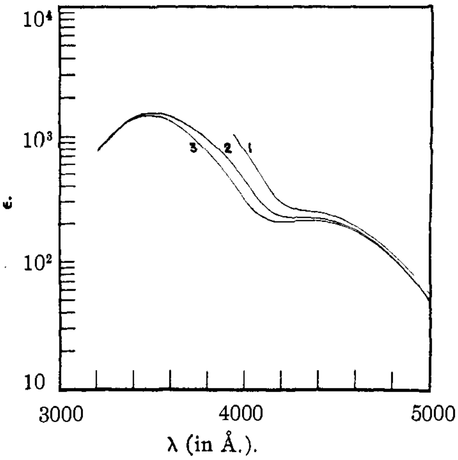

Fig. 1.—Apparent extinction coefficient, ϵ, of chromium(VI) at 25° in 1 M perchloric acid; chromium(VI) concentration (in gram-atoms per liter): 1, 1.79×10^{-2}; 2, 1.79×10^{-3}; 3, 1.79×10^{-4}.

The solutions which were used in the spectral studies were prepared by making known dilutions of the standard stock solutions.

Light Absorption Measurements.—The optical density of the solutions was determined using a model DU Beckman spectrophotometer. Measurements were made using cell lengths between 0.1 and 10 cm. The two smallest cell lengths (0.103 and 0.303 cm.) were realized using one-cm. cells and the quartz inserts manufactured by the Pyrocell Manufacturing Company.

The cells of two cm. length or greater were maintained at constant temperature with a special cell holder. The "Thermospacer" arrangement manufactured by the Beckman Instrument Co. was also used; this was the only means of maintaining temperature control when using the one-cm. cells. In all cases, however, the solution to be measured was kept at 25° until immediately before use. The temperature control was probably to within ±0.2° of 25°. The results of several experiments in which the temperature was 30° indicate that this uncertainty of ±0.2° has a negligible effect upon the value of $\bar{\epsilon}$ for a solution which contains an appreciable amount of both monomer and dimer.

At a particular wave length, the same slit width was used in all measurements. These widths were 0.04 mm. at 400 mμ without the use of the filter and 0.07 mm. at 390–370 mμ using the filter. It was shown, however, that the observed optical density values do not depend upon slit width. Duplicate readings on the same solution generally agreed within 0.5%. The optical density values obtained in this study were generally maintained in the range 0.3 to 0.7 by the use of the various cell lengths with the several concentrations of chromium(VI).

The Evaluation of K_d, ϵ_{11} and ϵ_{20}.—The equilibrium quotient, K_d, for reaction 2 is conveniently determined in media of an acidity which is low enough that inappreciable amounts of H_2CrO_4 and $HCr_2O_7^-$ are present and high enough that inappreciable amounts of $CrO_4^=$ are present. A series of 15 solutions with the composition 3.6×10^{-5} to 2.7×10^{-3} M potassium dichromate, 1.35×10^{-3} M perchloric acid, and 0.998 M lithium perchlorate was investigated. Since reaction 2 does not involve hydrogen ion, the concentration of hydrogen ion in all of these solutions is the same (1.35×10^{-3} M) even though the relative amounts of $HCrO_4^-$ and $Cr_2O_7^=$ change. The values of $\bar{\epsilon}$, the apparent extinction coefficient of chromium(VI), observed for this series of solutions are presented in Fig. 2. The trend is consistent with the existence of the equilibrium represented by equation 2. If the only species which are present at significant concentrations and which absorb appreciable light are

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(6) H. S. Harned, THIS JOURNAL, **48**, 326 (1926).

(7) E. Glueckauf, *Nature*, **163**, 414 (1949).

TABLE II

VALUES OF K', $\bar{\epsilon}_1$ AND $\bar{\epsilon}_2$ AS A FUNCTION OF THE CONCENTRATION OF PERCHLORIC ACID

$(HClO_4)$	1.35×10^{-3}	0.277	0.416	0.693	1.00
$(LiClO_4)$	0.998	0.723	0.584	0.306	0.00
No. of soln. studied	15	15	16	17	24
Range of C	7.2×10^{-5} to 5.4×10^{-3}	5.1×10^{-5} to 5.8×10^{-3}	5.1×10^{-5} to 5.8×10^{-3}	5.1×10^{-5} to 5.8×10^{-3}	3.6×10^{-5} to 0.013
K' ("Best" value)	98[a]	87	81	73	62
K' (from eq. 8)	98[a]	86	81	72	64
ϵ_1 380 mμ	792[b]	764	757	739	725
ϵ_1 390 mμ	519[b]	501	493	482	472
ϵ_1 400 mμ	326[b]	314	310	302	297
ϵ_2 380 mμ	2077[c]	2076	2078	2095	2072
ϵ_2 390 mμ	1740[c]	1733	1741	1746	1742
ϵ_2 400 mμ	1162[c]	1152	1162	1167	1174
Av. % difference[d]	0.36	0.24	0.34	0.38	0.48

[a] Since H_2CrO_4, $HCr_2O_7^-$ and $CrO_4^=$ are unimportant at this acidity, K' is the same as K_d; this is a value of K_d. [b] For the reasons given in [a], these are values of ϵ_{11}. [c] For the reasons given in [a], these are values of ϵ_{20}. [d] This is the average percentage difference between the observed values of $\bar{\epsilon}$ and the values calculated using the values of $\bar{\epsilon}_1$ and $\bar{\epsilon}_2$ presented in this table and the value of K' calculated using equation 8.

$HCrO_4^-$ and $Cr_2O_7^=$, the value of $\bar{\epsilon}$ is given by the equation

$$\bar{\epsilon} = \epsilon_{11}(1 - y) + \epsilon_{20}y \qquad (3)$$

The relationship between y, C and K_d is

$$2K_dC = y/(1 - y)^2 \qquad (4)$$

While it is possible to combine equations 3 and 4 to give a single equation involving the unknown quantities ϵ_{11}, ϵ_{20} and K_d, and the known quantities $\bar{\epsilon}$ and C, this equation is not particularly useful. An approximation method has been used to evaluate ϵ_{11}, ϵ_{20} and K_d. One first *assumes* a value of K_d; with the *assumed* value of K_d it is possible to evaluate the y value corresponding to each concentration of chromium(VI), C, which was studied.[8] For each experiment, there is an equation of the form of equation 3. The 15 such equations were solved by the method of averages.[9] This procedure was carried out for a number of *assumed* values of K_d. The average of the percentage difference between the observed values of $\bar{\epsilon}$ and the values calculated using equation 3 was considered to be a measure of the correctness of the K_d value which was assumed, and with which the values of y, ϵ_{11} and ϵ_{20} are consistent. Figure 3 summarizes the results of the calculations using the data at 1.35×10^{-3} M hydrogen ion. It is concluded that $K_d = 98$ at 25° and unit ionic strength, and that the values of ϵ_{11} and ϵ_{20} are those given in column 1 of Table II. The variation of $\bar{\epsilon}$ with chromium(VI) concentration is not as great at 370 mμ and these data (shown in Fig. 2) were not used in the evaluation of K_d; the use of these data is described in a later section of this paper.

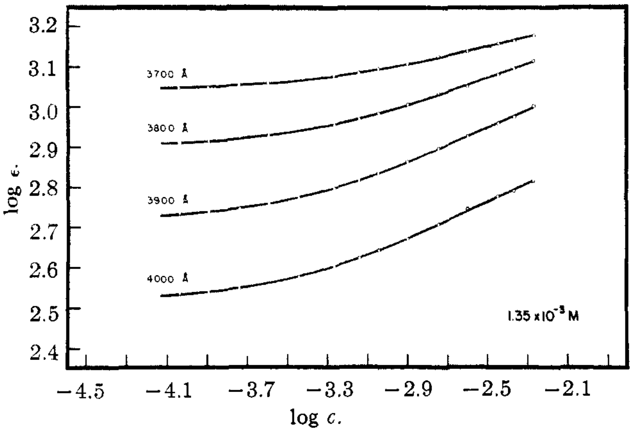

Fig. 2.—Logarithm of $\bar{\epsilon}$, the apparent extinction coefficient of chromium(VI), as a function of the concentration of chromium(VI) in gram-atoms per liter; each of the solutions had the composition: 1.35×10^{-3} M $HClO_4$ and 0.998 M $LiClO_4$.

The Evaluation of K_{11}, K_{22}, ϵ_{12} and ϵ_{21}.—Four series of experiments, similar to the series summarized in Fig. 2, were performed at 0.277, 0.416, 0.693 and 1.00 M perchloric acid. (The ionic strength was maintained at one with lithium perchlorate.) The variation in $\bar{\epsilon}$ with C at these acidities is qualitatively the same as was observed at 1.35×10^{-3} M hydrogen ion (presented in Fig. 2). Treatment of the data obtained at each of these higher acidities in the same manner as was used at 1.35×10^{-3} M hydrogen ion yields, for each particular acidity, the values of K', the gross dimerization quotient, $\bar{\epsilon}_1$, the apparent extinction coefficient of chromium(VI) monomers and $\bar{\epsilon}_2$, the apparent extinction coefficient of chromium(VI) dimers. The values of these quantities are summarized in Table II. The "best" value of K' at each acidity was assumed to be the average of the "best" values determined at each wave length using the criterion already mentioned. The values of $\bar{\epsilon}_1$ and $\bar{\epsilon}_2$ are those corresponding to the value of K' calculated using equation 8 and not the value of K' which gave the best agreement at that wave length alone. The difference between the values of $\bar{\epsilon}_1$ and $\bar{\epsilon}_2$ presented in Table II and the corresponding values which give the best agreement using the K' value best fitting the data at each wave length is small; the average value of this difference is 0.1% for $\bar{\epsilon}_1$ and 1.4% for $\bar{\epsilon}_2$.

If, in this range of acidity, the only monomeric chromium(VI) species was $HCrO_4^-$ and the only dimeric chromium(VI) species was $Cr_2O_7^=$, the values of K', $\bar{\epsilon}_1$ and $\bar{\epsilon}_2$ determined at each acidity would be equal to the values of K_d, ϵ_{11} and ϵ_{20}, respectively. An examination of the values of these quantities presented in Table II reveals that K' and $\bar{\epsilon}_1$ are functions of the hydrogen ion concentration while $\bar{\epsilon}_2$ shows no significant trend. Thus, the spectral data demonstrate that species of chromium(VI) other than $HCrO_4^-$ and $Cr_2O_7^=$ are important at these higher acidities.

Since $\bar{\epsilon}_1$ varies with a change in the hydrogen ion concentration, the species H_2CrO_4 must be present at significant concentrations in the range 0.28–1.0 molar hydrogen ion. The relevant equation for the evaluation of ϵ_{12} and K_{11} from the values of $\bar{\epsilon}_1$ as a function of acidity is

$$\bar{\epsilon}_1[(HCrO_4^-) + (H_2CrO_4)] = \epsilon_{11}(HCrO_4^-) + \epsilon_{12}(H_2CrO_4) \qquad (5)$$

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[8] Since it would be tedious to solve equation 4 for the y value corresponding to each experimental concentration for each assumed value of K_d, tables of $F(y)$ (defined in Table I) for y values in the range 0.600–0.001 have been prepared. The difference between the y value of the successive entries is 0.002 (y = 0.600 to 0.100), 0.001 (y = 0.100 to 0.010), and 0.0002 (y = 0.010 to 0.0010). It is possible, with these tables to obtain by interpolation the value of y for any value of $F(y)$ (*i.e.*, for any value of $2K_dC$) with a precision of ±0.01%.

[9] F. Daniels, J. H. Mathews and J. W. Williams, "Experimental Physical Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1949, p. 369.

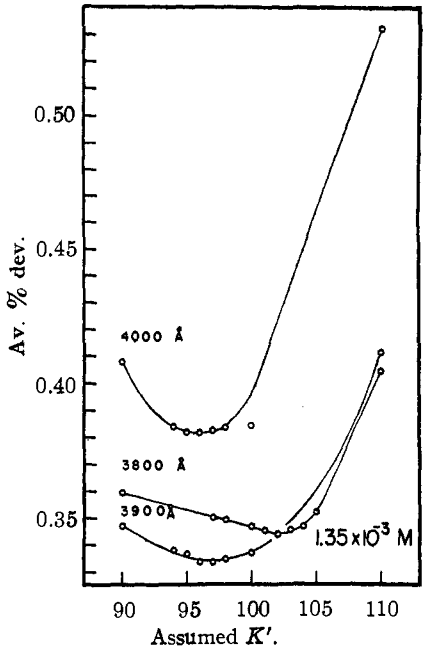

Fig. 3.—The average percentage deviation between the observed values of $\bar{\epsilon}$ and the values calculated using an assumed value of K' and the $\bar{\epsilon}_1$ and $\bar{\epsilon}_2$ values associated with that assumed value of K' vs. the assumed value of K'. The "best" value of K' at this acidity (1.35×10^{-3} M H^+) was chosen as 98. At this acidity, K' is equal to K_d.

which leads to

$$\epsilon_1 = \epsilon_{12} + \frac{K_{11}(\epsilon_{11} - \epsilon_1)}{(H^+)} \tag{6}$$

a linear equation in the two unknowns, K_{11} and ϵ_{12}. A least square treatment of the four values of $\bar{\epsilon}$ at each wave length leads to the values of K_{11} which are presented in Table III. The average of these values is 1.21, which was chosen as the value of K_{11} at 25° in a medium of unit ionic strength. The values of ϵ_{12} which are presented in Table III are the average values calculated using equation 6 and 1.21 as K_{11}. The graphs in Fig. 4 show the lines calculated using these parameters.

TABLE III

VALUES OF K_{11} AND ϵ_{12} DETERMINED FROM THE VARIATION OF $\bar{\epsilon}_1$ WITH ACIDITY

Wave length	400 mμ	390 mμ	380 mμ
K_{11}	1.22	1.28	1.12
ϵ_{12}	262	412	654
Av. % difference[a]	0.1	0.2	0.3

[a] This is the average percentage difference between the values of $\bar{\epsilon}_1$ determined at the five acidities (see Table II) and the values calculated using equation 6 with $K_{11} = 1.21$, the values of ϵ_{12} listed here and the values of ϵ_{11} presented in Table II.

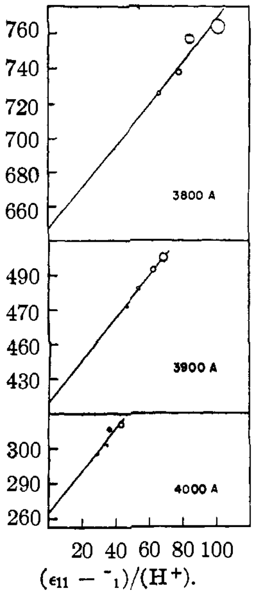

Fig. 4.—The apparent extinction coefficient of chromium(VI) monomeric species, $\bar{\epsilon}_1$, vs. $(\epsilon_{11} - \bar{\epsilon}_1)/(H^+)$. The slope of the line is the value of K_{11} and the intercept is the value of ϵ_{12} (equation 6).

The lack of a significant variation of $\bar{\epsilon}_2$ with the acidity of the solution does not mean that a single dimer species of chromium(VI) exists in solution throughout this range of acidity. There might be more than one species involving different numbers of hydrogen ions and yet the value of $\bar{\epsilon}_2$ would be independent of acidity even though the relative amounts of the species were changing, if these species had approximately the same extinction coefficients at the wave lengths studied.[10] The existence of $HCr_2O_7^-$ in the acidity range 0.277–1.00 M may be demonstrated from the variation of K' with acidity. If $HCr_2O_7^-$ did not exist to an appreciable extent in this acidity range, the equation

$$K' = K_D\left\{\frac{K_{11}}{K_{11} + (H^+)}\right\}^2 \tag{7}$$

would give the dependence of K' upon the concentration of hydrogen ion. Figure 5 shows the empirical values of K' and the values calculated using equation 7 with the values of K_{11} and K_D equal to 1.21 and 98, respectively. The large discrepancy can be removed if one assumes that $HCr_2O_7^-$ is present in these solutions; under such conditions, the equation

$$K' = K_D\left\{\frac{K_{11}}{K_{11} + (H^+)}\right\}^2\left\{\frac{K_{22} + (H^+)}{K_{22}}\right\} \tag{8}$$

gives the dependence of K' upon acidity. A value of K_{22} can be calculated from the value of K_{11} and each set of values of K' and (H^+). The average value of K_{22} so calculated is 0.85. The solid line in Fig. 5 shows the variation of the value of K' with acidity given by equation 8. The introduction of this additional parameter, K_{22}, completely correlates the variation of K' with acidity.

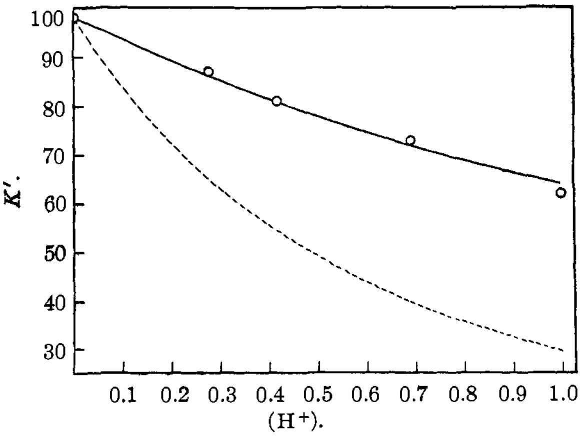

Fig. 5.—The value of K' as a function of the acidity. The dashed line is that calculated using equation 7 and the solid line is that calculated using equation 8.

It is to be noted that the concentration of chromium(VI) in all of these solutions is low enough that in combining with

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[10] The wave lengths at which measurements were selected with the goal of realizing as large a change of $\bar{\epsilon}$ with a change of the concentration of chromium(VI) as was possible. It is possible that at some other wave length, the variation of $\bar{\epsilon}_2$ with acidity is significant.

hydrogen ion to form H_2CrO_4 or $HCr_2O_7^-$, it does not alter the concentration of hydrogen ion from the value obtained by considering the amount of perchloric acid added.

The method of treatment of the data has allowed the calculation of the several parameters in a stepwise manner. It is possible to make a comparison between the values of K' calculated using equation 8 and those considered to be the "best" values; this is done in Table II. At the acidities 1.35×10^{-3}, 0.277, 0.416, 0.693 and 1.00 M hydrogen ion concentration, 260 values of the optical density have been determined. These optical density values are for solutions in which the extents of the contribution of the several chromium(VI) species are: H_2CrO_4, 0–45%; $HCrO_4^-$, 30–99%; $HCr_2O_7^-$, 0–25%; $Cr_2O_7^=$, 0–39%. In the correlation of these data, a total of twelve parameters K_d, K_{11}, and K_{22} and nine extinction coefficients, ϵ_{11}, ϵ_{12} and $\bar{\epsilon}_2$ at the three wave lengths are available. (The $\bar{\epsilon}_2$ value at each wave length was chosen as the average of the values determined at the several acidities.) The average of the difference between the observed and the calculated values of $\bar{\epsilon}$ for all of these solutions is 0.4%. This is considered to be excellent agreement. The uncertainty in the values of the several equilibrium quotients is considerably larger than is suggested by this agreement, however. The reason for this is the fact that the chromium(VI) and hydrogen ion concentration ranges, while large, are not large enough to make each of the several chromium(VI) species dominant under some of the concentration conditions. The maximum fraction of chromium (VI) present as dimeric species in the series of experiments at 1.35×10^{-3}, 0.277, 0.416, 0.693, and 1.00 molar perchloric acid is 0.39, 0.38, 0.37, 0.35 and 0.47, respectively. At the highest concentration of hydrogen ion studied (1.00 molar), 45% of the monomeric chromium(VI) is present as H_2CrO_4 and 54% of the dimeric chromium(VI) is present as $HCr_2O_7^-$. By the use of cells with a shorter light path and the adoption of a higher ionic strength value at which to maintain the medium, one could realize measurements on solutions of higher concentrations of chromium(VI) and hydrogen ion.

Measurements at 370 mμ and at 0.1386 M Perchloric Acid.—In addition to the data which have been presented, the optical densities of the solutions were determined at 370 mμ. Since the variation of $\bar{\epsilon}$ with the concentration of chromium(VI) is less pronounced than it is at 380–400 mμ, these data are of less value in establishing the values of K_d, K_{11} and K_{22}. Rather than use the data at 370 mμ in the same manner as the data at longer wave lengths, the observed values of $\bar{\epsilon}$ were used in conjunction with the values of the three equilibrium quotients already evaluated in order to determine the several extinction coefficients. The values of ϵ_{11} and ϵ_{20} were calculated using the value of K_d and the data at 1.35×10^{-3} molar hydrogen ion. The values of $\bar{\epsilon}_1$ and $\bar{\epsilon}_2$ were calculated for the other acidities by the use of the value of K' calculated using equation 8. The calculation of the value of ϵ_{12} from the trend in the value of $\bar{\epsilon}_1$ as a function of acidity was possible since ϵ_{11} and K_{11} were known. As was true at the other wave lengths, the value of $\bar{\epsilon}_2$ does not vary with acidity. The values of ϵ_{11}, ϵ_{12}, and $\bar{\epsilon}_2$ at 370 mμ are 1100, 910, and 2140, respectively. The use of these values and the equilibrium quotient values already mentioned leads to calculated values of $\bar{\epsilon}$ with an average deviation of 0.4% from the observed values.

In addition, the optical densities of a series of thirteen solutions with a chromium(VI) concentration range of 5.0 $\times 10^{-5}$ to 5.8×10^{-3} gram atoms per liter, 0.1386 molar perchloric acid and 0.861 molar lithium perchlorate were determined at 370, 380, 390 and 400 mμ. The observed values of $\bar{\epsilon}$ were compared with the values calculated with the equilibrium quotients and the extinction coefficients which were established using the data already presented. The average deviation between the observed and calculated values of $\bar{\epsilon}$ is 0.9%.

The Value of K_d as a Function of the Ionic Strength.—The values of the equilibrium quotients, K_d, K_{11} and K_{22} which have been obtained are expected to be strictly valid only for the media in which they were determined (*i.e.*, a solution of unit ionic strength containing primarily perchloric acid and lithium perchlorate). In solutions of other electrolytes with the same ionic strength, the values of the equilibrium quotients may be different. The extent of the variation to be expected in media of constant ionic strength but varying composition is difficult to estimate; an examination of existing data indicates that it can be appreciable.[6,11] It is desirable to obtain data which allow an extrapolation of the values of these equilibrium quotients to zero ionic strength. The evaluation of K_{11} and K_{22} is possible, however, only in media in which the hydrogen ion concentration is appreciable compared to magnitude of these equilibrium quotient values, 1.21 and 0.85, respectively. Thus, it is not possible to perform experiments which will lead to the values of these two equilibrium quotients near zero ionic strength. The evaluation of K_d, on the other hand, can be conveniently made in media of low ionic strength.

The simplest approach to the evaluation of K_d at other values of the ionic strength involves the use of the ϵ_{11} and ϵ_{20} values which were established in the runs at unit ionic strength. It was desirable, therefore, to ascertain whether these extinction coefficient values vary appreciably with ionic strength. The optical density values of solutions which are 10^{-3} M hydrogen ion and as dilute as 4×10^{-5} gram-atoms of chromium(VI) per liter lead directly to the values of $\bar{\epsilon}$ which are very close to the values of ϵ_{11}, since at this concentration the dimeric chromium(VI) species is present to the extent of less than one per cent. in a medium of unit ionic strength. Three solutions, 1.99 M, 0.99 M and 0.00 M in sodium perchlorate and each containing 1.3×10^{-3} M perchloric acid and 4.1×10^{-5} gram-atom per liter of chromium(VI), yielded 3 values of $\bar{\epsilon}$ at 390 mμ which agree with a maximum difference of 1%. The average of these values differed by 3.5% from 519, the value of ϵ_{11} at 390 mμ determined in the experiments at unit ionic strength. One half of this difference is due to the presence of the small equilibrium amount of $Cr_2O_7^=$.

The investigation of the possible dependence of the value of ϵ_{20} upon the ionic strength is not as direct since the highest concentration of chromium(VI) which is conveniently studied corresponds to the presence of a significant amount of monomeric chromium(VI) species. Optical density measurements at 390 mμ were made upon two series of solutions, one series at ionic strength 0.50 and the other at ionic strength 2.00, the ionic strength being primarily due to sodium perchlorate. All of the solutions were 1.3 × 10^{-3} molar perchloric acid and each series included five solutions with a chromium(VI) concentration range of 8.3 $\times 10^{-4}$ to 6.6×10^{-3} gram atom per liter. The value of K_d was calculated from the observed value of $\bar{\epsilon}$ for each solution using the ϵ_{11} and ϵ_{20} values determined in the experiments at unit ionic strength. If the ϵ_{20} value was not correct, the K_d values would vary in a regular manner as the chromium(VI) concentration changed since the relative amounts of monomeric and dimeric species varied with the chromium(VI) concentration. Such is not the case; no regular trend in the values of K_d was observed. In the series at ionic strength 0.50, the value of K_d is 79 ± 1; in the series at ionic strength 2.00, the value of K_d is 125 ± 3. It seems reasonable therefore to assume that both ϵ_{20} and ϵ_{11} are independent of the ionic strength up to 2.0 molar.

The dependence of K_d upon the ionic strength has been established in sodium perchlorate solutions with a hydrogen ion concentration of 1.35×10^{-3} molar and in sodium sulfate–sodium bisulfate solutions with a measured pH value of 3.00 ± 0.02. The concentration of chromium(VI) was 4 to 6×10^{-3} gram atom per liter in most experiments. The values of $\bar{\epsilon}$ were determined at 370, 380, 390 and 400 mμ; with equation 3 and the known values of ϵ_{11} and ϵ_{20}, it is possible to calculate y, which may then be used in equation 4 to calculate the value of K_d. The values of K_d arising from $\bar{\epsilon}$ values determined at different wave lengths agree very well, 1.3% being the over-all average of the percentage difference between the values obtained at the several wave lengths and the average of these values.

The values of K_d are presented in Fig. 6, in which log K_d is plotted *versus* $\sqrt{\Gamma/2}/(1 + 1.5\sqrt{\Gamma/2})$. The K_d values obtained in sodium perchlorate solutions up to an ionic strength of 0.6 have an average deviation from the straight line of 1.5%. The coefficient of $\sqrt{\Gamma/2}$ in the denominator was chosen by successive approximations which lead to a line of the theoretical slope. For a reaction of this charge type, the theoretical slope is 1.01; least square treatment of the data obtained in sodium perchlorate media up to an

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[11] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1950, Chap. 14.

ionic strength of 0.6 has given the solid line which is shown in Fig. 6. This line has a slope of 1.01 and an intercept which corresponds to $K_d^\circ = 35.5$; the equation for the line is

$$\log K_d = 1.55 + \frac{1.01\sqrt{\Gamma/2}}{1 + 1.5\sqrt{\Gamma/2}}$$

This value and the value 43 obtained by Neuss and Rieman[4] are in substantial agreement. These authors' data are also presented in Fig. 6. It is believed that the approach to the problem which has been used in this work is the more direct one and therefore the K_d values determined spectrophotometrically are believed to be subject to a smaller uncertainty. Since the solutions studied by Neuss and Rieman contained potassium chloride, it might be suggested that chlorochromate ion, $ClCrO_3^-$, studied by Cohen and Westheimer[12] is present to an appreciable extent in the solutions which they studied. Although this possibility cannot be ruled out (the equilibrium quotient for the reaction $H^+ + Cl^- + HCrO_4^- = ClCrO_3^- + H_2O$ is 1.1×10^5 in 86.5% acetic acid), the acidity of the solutions studied by Neuss and Rieman (pH $\cong$ 6) was such as to suggest that $ClCrO_3^-$ was not present at an appreciable concentration.

It is seen that the values of K_d determined in sulfate media with a measured pH of 3.00 ± 0.02 agree moderately well with the values obtained in sodium perchlorate solutions with a hydrogen ion concentration of 1.35×10^{-3} molar. The values of K_d obtained in sulfate media depend upon the measured pH value of the solution even though at this concentration of hydrogen ion, the value of K' is very nearly equal to K_d and should not be sensitive to small changes in the concentration of hydrogen ion. The cause of this anomaly may be the existence, at very low concentrations, of species containing sulfur(VI) and chromium (VI). Such species are not completely unexpected in view of the demonstration of the existence of the phosphorus (V)-chromium(VI) species by Holloway.[13]

Discussion

The magnitude of the equilibrium quotients for the ionization of chromium(VI) acids is worthy of mention. It is first to be noted that the ionization constants of HSO_4^- and $HCrO_4^-$ differ by a factor of 3×10^4 (0.010 for HSO_4^- and 3.2×10^{-7} for $HCrO_4^-$). The ionization constant of bisulfate ion is nicely correlated with the formal charge on the central atom by the equation presented by Ricci[14]; the acids which Ricci's equation correlates do not include any with a transition element as the central atom. If the type of bonding between the chromium and oxygen in chromate ion were the same as the type of bonding between sulfur and oxygen in sulfate ion, these two ionization constants might be expected to be very similar. Wolfsberg and Helmholz[15] have considered the electronic structures of MnO_4^-, $CrO_4^=$ and ClO_4^-, and they conclude that in the case of the ions involving the transition elements, all five 3d orbitals and the 4s orbital are employed in bonding, whereas in ClO_4^-, the 3d atomic orbitals have very small coefficients in the bonding molecular orbitals in their approximation calculation. It would be expected that the bonding in sulfate ion resembles that in perchlorate ion. Thus, there is a large difference in the nature of the central atom-oxygen bond in these species which is reflected in a difference of the tendency for other atoms to be bonded to the $XO_4^=$ ion. In addition to the difference in the tendency to form HXO_4^-, there is the difference in the tendency to form $X_2O_7^=$. While $Cr_2O_7^=$ forms at relatively low concentrations of chromium(VI), the corresponding sulfur(VI) species does not exist except under the most drastic concentration conditions. On the basis of the values observed for oxygen acids in which the central atom is not a transition element,[14] one would predict a factor of 10^4 for the ratio of $K_{H_2CrO_4}/K_{HCrO_4^-}$; the observed value of this ratio is $1.21 \times 0.5/3.2 \times 10^{-7} = 2 \times 10^6$ (the value of K_{11} obtained in this work at unit ionic strength is multiplied by 0.5 in order to convert it to a value at zero ionic strength; the basis for this correction is the observed effect of lithium chloride upon the ionization quotient for acetic acid[16]). It is seen that the ratio of the two ionization constants for H_2CrO_4 differ by a factor which is considerably larger than is observed for many oxygen acids in which the central atom is not a transition element. This discussion is designed merely to point out certain differences between chromate ion and sulfate ion and to suggest the obvious extrapolation that marked differences may be expected between certain properties of oxygenated anions of the transition elements and analogous anions of the non-transition elements.

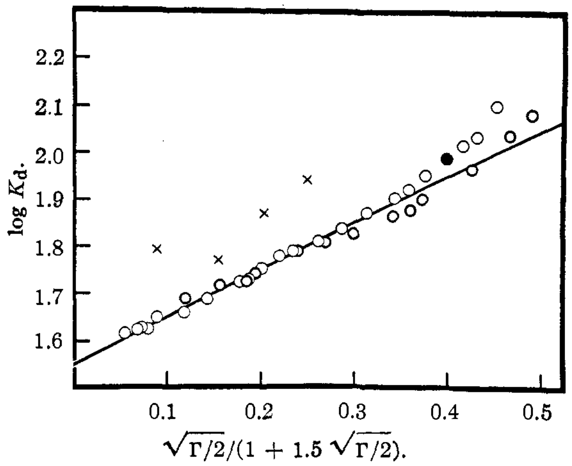

Fig. 6.—Logarithm K_d *vs.* $\sqrt{\Gamma/2}/(1 + 1.5\sqrt{\Gamma/2})$. The open circles, O, are points determined in sodium perchlorate-perchloric acid solutions. The double circles, ◎, are points determined in sodium sulfate—sulfuric acid solution. The solid point, ●, is the average value of the fifteen experiments in lithium perchlorate—perchloric acid solution. The crosses, X, are from the work of Neuss and Rieman.[4]

It is of interest to note that the values of the acid ionization quotients for H_2CrO_4 and $HCr_2O_7^-$ are about the same ($K_{11} = 1.21$ and $K_{22} = 0.85$). A similarity is also observed between certain of the acid ionization quotients for phosphoric acid and pyrophosphoric acid,[17] the correspondence being between the acid strengths of $H_nPO_4^{n-3}$ and $H_nP_2O_7^{n-4}$ (*i.e.*, $K_{H_3PO_4} = 7.5 \times 10^{-3}$ and $K_{H_3P_2O_7^-} = 11 \times 10^{-3}$; $K_{H_2PO_4^-} = 6.2 \times 10^{-8}$ and $K_{H_2P_2O_7^=} = 21 \times 10^{-8}$; $K_{HPO_4^-} = 10^{-12}$ and $K_{HP_2O_7^\equiv} = 4.1 \times 10^{-10}$). One is tempted to generalize and suggest that the K value for a dimeric acid formed by splitting one water molecule out of two monomeric acid molecules is approximately

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[12] M. Cohen and F. H. Westheimer, THIS JOURNAL, **74**, 4387 (1952).

[13] F. Holloway, *ibid.*, **74**, 224 (1952).

[14] J. E. Ricci, *ibid.*, **70**, 109 (1948).

[15] M. Wolfsberg and L. Helmholz, *J. Chem. Phys.*, **20**, 837 (1952).

[16] H. S. Harned and F. C. Hickey, THIS JOURNAL, **59**, 2303 (1937).

[17] D. M. Yost and H. Russell, "Systematic Inorganic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1944, p. 228.

equal to the K value of the monomeric acid with one less unit of negative charge.

Throughout this paper, the formula of the dimeric chromium(VI) species which is predominant at *p*H 3 has been represented as $Cr_2O_7^{=}$. The data obtained in this study establish only the number of chromium(VI) atoms in the species (two) and the charge on the species (minus two). A representation as $(HCrO_4^-)_2$ would be equally good as far as these data are concerned. These two formulas $Cr_2O_7^{=}$ and $(HCrO_4^-)_2$ differ by one molecule of water and, as is often true, the determination of the extent of hydration of ionic species in aqueous solution can be very difficult. If the rate of exchange of O^{18} between solvent water and the oxygenated chromium(VI) species proves to be measurable, the results will be of value in connection with this question; such results have been of value in other such problems.[18]

(18) H. W. Crandall, *J. Chem. Phys.*, **17**, 602 (1949); J. P. Hunt and H. Taube, *ibid.*, **19**, 602 (1951).

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF RUTGERS UNIVERSITY]

Polyphosphates as Polyelectrolytes. II. Viscosity of Aqueous Solutions of Graham's Salts[1]

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The viscosity behavior of aqueous solutions of several samples of sodium polyphosphate, covering a molecular weight range from 7000 to 19000, was investigated. The results for each sample could be represented by the Fuoss equation, $\eta_{sp}/C = A/(1 + B\sqrt{C}) + D$. The parameters A, B and D all increased with molecular weight. The intrinsic viscosity, $A + D$, was proportional to the 1.87th power of the molecular weight, indicating rod-like structure of the polyions at infinite dilution. The end-to-end distances of the polyions at infinite dilution, estimated from the intrinsic viscosity values, were of the same order of magnitude as their contour lengths, calculated from the molecular weights, confirming the absence of chain branching of these polyelectrolytes in solution.

In a previous paper, the viscosity and light scattering behavior of several samples of Graham salt in electrolyte solutions was reported.[2] The work was initiated for two reasons: first, in order to determine the molecular dimensions of these useful inorganic polyelectrolytes; second, in order to learn more about the behavior of polyelectrolytes. In the present paper a continuation of this study is presented, which deals with the viscosity behavior of the same Graham salt samples in pure water.

Experimental

The preparation of the eight samples of sodium polyphosphate, covering a molecular weight range from 7000 to 19,000, has been described.[2]

Viscosities were measured at 25° in the same Bingham viscometer and by the same procedure as was used previously.[2] Since the viscosities of the freshly prepared solutions decreased for about 12 hours after dissolution, all measurements reported in this paper were taken after this period, *i.e.*, when the viscosities had become constant. The soundness of this procedure has been established.[2] All viscosity results were found to be independent of the velocity gradient which was varied between about 2000 and 5000 sec.$^{-1}$.

Results and Discussion

The viscosity behavior of each sample was typical of flexible polyelectrolytes and could be accurately represented by the equation of Fuoss[3]

$$\frac{\eta_{sp}}{C} = \frac{A}{1 + B\sqrt{C}} + D \qquad (1)$$

where C is the concentration in grams of solute per 100 ml. of solution, η_{sp}/C is the reduced viscosity, and A, B and D are constants characteristic of each sample. The data were fitted to this relation in the usual manner, by plotting $(\eta_{sp}/C - D)^{-1}$ against $C^{1/2}$, D being first approximately obtained from a plot of η_{sp}/C against $C^{-1/2}$ [4] and then adjusted to make the $(\eta_{sp}/C - D)^{-1}$ *vs.* $C^{1/2}$ curve perfectly linear. Three representative lines are shown in Fig. 1. From the intercepts, $1/A$, and the slopes, B/A, the constants A and B have been calculated. All the parameters of eq. 1 are collected in Table I. The molecular weights which are given in the second column for comparison were previously obtained by light scattering.[2,5]

TABLE I

FUOSS EQUATION PARAMETERS

Sample	M	D	$1/A$	B/A	A	B	$[\eta]$ in 0.35 N NaBr
134	7400	0.06	0.30	6.37	3.3	21	0.066
169	9800	.08	.20	4.57	5.0	23	
181	9900	.08	.13	4.17	7.7	32	
242	14000	.08	.10	2.77	10	28	.086
270	15800	.095	.06	2.40	17	40	
305	17100	.12	.06	2.11	17	35	
309	17400	.12	.05	2.07	20	41	
312	18200	.095	.06	2.00	17	33	.101

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(1) This investigation was supported by a grant from the United States Atomic Energy Commission under Contract AT(30-1)1018. Most of the contents of this article formed part of a paper presented before the Division of Polymer Chemistry of the American Chemical Society, Atlantic City, New Jersey, September, 1952.

(2) U. P. Strauss, E. H. Smith and P. L. Wineman, THIS JOURNAL, **75**, 3935 (1953).

(3) R. M. Fuoss, *J. Polymer Sci.*, **3**, 603 (1948); correction, *ibid.* **4**, 96 (1949).

(4) W. N. Maclay and R. M. Fuoss, *ibid.*, **6**, 511 (1951).

(5) Incidentally, an empirical relationship between the viscosity of aqueous polyphosphate solutions and the molecular weight as determined by end-group titrations recently has been reported [R. Pfanstiel and R. K. Iler, THIS JOURNAL, **74**, 6059 (1952)]. Applying this relationship to our viscosity data, we find molecular weights about 60% of the light scattering values. This is of the right order of magnitude, considering the polydispersity of the samples and the different molecular weight averages measured by end-group titrations on the one hand (number-average) and by light scattering on the other (weight-average).