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A Light-Scattering Study of Acidified Sodium Tungstate Solutions[1]

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Upon acidification with strong acid at room temperature the aggregation of normal tungstate ions to isopolytungstate ions is shown to result in unstable, yet very long half-lived polyions. The average degree of aggregation of the species formed at $H^+:WO_4^{2-}$ of 9:6 is sixteen. The solutions come to equilibrium at 50° in about 6 days. Acidification of normal tungstate ions with acetic acid–acetate buffer does not give rise to the large, unstable isopolyanions, but results, in the 9:6 solutions, in rapid formation of the equilibrium dodecatungstate ion.

Introduction

The state of knowledge of isopolytungstate ion formation up to 1962 has been adequately reviewed by Kepert.[2] Very recently Aveston[3] studied acidified tungstate solutions by equilibrium ultracentrifugation at 50°, by acidity measurements at 50°, and by Raman spectroscopy at *ca.* 35°. Simultaneously we conducted a study of the same system by light scattering at 25°. Even at 50° Aveston reports relatively slow approach to equilibrium in some of his preparative procedures. Our results, in essential agreement with those of Aveston, show that most solutions of isopolytungstates, made and kept at 25°, approach equilibrium with halftimes of the order of weeks or months. Thus, while we believe that the one hexatungstate and two dodecatungstate species of Aveston account well for the properties of acidified tungstate solutions at equilibrium, it is now important to point out that the approach to equilibrium in isopolytungstate solutions prepared at room temperature can be very slow indeed.

Experimental

Stock Solutions.—Reagent grade chemicals were used. Sodium tungstate 2-hydrate (Fisher Scientific or J. T. Baker) was recrystallized from water once and dissolved in distilled, demineralized water (used to prepare all subsequent solutions) to give solutions of final W(VI) concentration approximating 1 *M*. Perchloric acid solutions were prepared from J. T. Baker 70–72% acid by simple dilution. Baker and Adamson glacial acetic acid was diluted to make acetic acid stock solution. G. Frederick Smith sodium perchlorate was recrystallized twice from water and dissolved in sufficient water to make 5–6 *M* solutions. Qualitative tests showed no turbidity when treated with silver nitrate. J. T. Baker sodium acetate was recrystallized once and used to make an approximately 1 *M* stock solution.

Analyses.—Sodium tungstate, sodium perchlorate, and sodium acetate stock solutions were standardized by carefully evaporating aliquots to dryness and by dehydrating the residues at 250° in the case of the tungstate and at 110° in the cases of perchlorate and acetate. The perchloric and acetic acid stock solutions were standardized volumetrically using potassium hydrogen phthalate as the primary standard.

Sodium paratungstate crystals obtained from many of the solutions studied were analyzed by the method of Saddington and Cohn.[4] The water content of the crystals was taken as equal to the loss in weight of samples heated to 300°. The sodium content was determined by heating samples at 500–550° in an atmosphere of hydrogen chloride, thereby converting all tungsten to volatile oxyhalides and all sodium to sodium chloride, which was weighed as such. The tungsten was estimated gravimetrically, using cinchonine, according to the procedure of Wilson and Wilson.[5]

Experimental Solutions.—Calculated amounts of stock solutions were delivered into 100-ml. volumetric flasks using calibrated burets. The normal order of addition of reagents was tungstate stock, sodium perchlorate stock, perchloric acid stock, and water to the mark. Some solutions were prepared by reversing the order of addition of the second and third reagents. The white tungstic acid which separated at the point in the solution where the acid entered disappeared rapidly when the solutions were stirred vigorously. In all cases, the reagents were added slowly with vigorous stirring, to avoid raising the temperature of the solutions appreciably above room temperature. Some solutions were prepared in still a third way by passing an aliquot of tungstate stock solution through a Dowex 50W-8X ion-exchange column in the H^+ form and adding the appropriate amount of standard sodium hydroxide to the eluent. Solutions made by the latter procedure had to be handled quickly before the colloidal tungstic acid coagulated to a gelatinous mass. In addition W(VI) analyses on the final solutions were performed since very small, but measurable amounts of W(VI) were retained in the resin bed. Some solutions were made up to a total supporting electrolyte concentration ($NaClO_4$) of 2 *M*. Other series were made up to 1 *M* $NaClO_4$. After preparation the solutions were kept in a room thermostated at 25 ± 1°. Refractive index and turbidity measurements on representative solutions made up in the three different ways gave the same results, indicating that the preparative variations do not result in different solutions in this case.

In this work a series is considered to be several solutions, each differing in total W(VI) concentration but all having the same molar ratio of acid added to tungstate. In calculating how much stock $NaClO_4$ to add to make up the proper total amount of $NaClO_4$ in a solution, it was considered that all of the $HClO_4$ added is converted to $NaClO_4$. Even in the 9:6 solutions the pH values were in the 3.5–4.0 range, indicating that substantially all of the $HClO_4$ was consumed as it was added in the preparation of experimental solutions. Enough additional stock $NaClO_4$ was added to make up the required amount. Each experimental solution was numbered. The number to the left of the decimal gives the molarity of the supporting electrolyte, $NaClO_4$. The last digit to the right of the decimal gives the ratio of moles of acid added per 6 moles of tungstate ion. The remaining digits to the right of the decimal give the molar concentration of W(VI). Thus solution 2.157 is 2 *M* in $NaClO_4$, 0.15 *M* in total W(VI), and was made up so that $H^+:WO_4^{2-}$ = 7:6. In 100 ml. of such a solution there are 200 mmoles of

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[1] From a dissertation submitted to the Graduate School of The University of North Carolina in partial fulfillment of the requirements for the Ph.D. degree, 1964.

[2] D. L. Kepert, *Progr. Inorg. Chem.*, **4**, 199 (1962).

[3] J. Aveston, *Inorg. Chem.*, **3**, 981 (1964).

[4] K. Saddington and R. W. Cohn, *J. Chem. Soc.*, 3526 (1950).

[5] C. L. Wilson and D. W. Wilson, "Comprehensive Analytical Chemistry," Elsevier Publishing Co., New York, N. Y., 1962, p. 601.

$NaClO_4$, $15 \times {}^7/_6 = 17.5$ of which came from the reaction of tungstate stock with perchloric acid stock. In making the same solution from tungstic acid (ion-exchange bed), ${}^5/_6 \times 15 = 12.5$ mmoles of NaOH would have been added to 15 mmoles of H_2WO_4, followed by the addition of 200 mmoles of $NaClO_4$.

The series studied correspond to $H^+:WO_4^{2-}$ = 0:6, 2:6, 4:6, 6:6, 7:6, 8:6, 9:6, 10:6, 11:6, and 12:6. The variation in W(VI) concentration was made tenfold where possible, *e.g.*, 0.03 to 0.30 *M*. This was not possible in all cases, since at very low concentrations for some series the signal-to-background turbidity ratio was too small. In others the upper limit was curtailed by the solubility of the isopolytungstate salt.

X-Ray Powder Photography.—Powder patterns of crystals were obtained using a 114.59-mm. Norelco powder camera with Cu Kα radiation.

Density and pH Measurements.—Densities were determined pycnometrically at 25°. The pH of each experimental solution was measured at 25° using a Leeds and Northrup pH meter standardized with a saturated solution of potassium hydrogen tartrate.

Turbidity Measurements.—The measurements were made on the instrument described previously.[6] We continue to use the value of 7.71×10^{-4} cm.$^{-1}$ for the turbidity of benzene, our secondary standard. In a given solution the gross turbidity, τ, is the summation of the background turbidity of the solvent, the turbidity due to the supporting electrolyte, and the turbidity of the W(VI) solute, τ^*. In each series τ was plotted as a function of M', the molar concentration of W(VI). The intercept at $M' = 0$ gave a turbidity due to solvent and $NaClO_4$, which checked very well with the measured turbidity of such an experimental solution. Subtraction of the turbidity so obtained from the actual experimental τ of each solution gave τ^* values. All measurements reported herein were made with 4358 Å. light. Solutions 1.19 and 1.17 were checked for dissymmetry of scattering using a cylindrical cell. No appreciable dissymmetry was found. These being fairly concentrated solutions at the highest $H^+:WO_4^{2-}$ ratios we presumed that all true solutions measured were behaving as simple Rayleigh scatterers. All other measurements were made in 3-cm. square cells.

Each solution was clarified prior to measurement by passage, under pressure of N_2 gas, through an ultrafine sintered glass filter. In general each solution was filtered and measured until two or more successive filtrations gave the same value.

Refractive Index Increments.—These magnitudes were determined using a Brice–Phoenix differential refractometer at 4358 Å. wave length.

Results and Discussion

In the quantitative interpretation of the light-scattering data we shall follow our previous procedure, this time for anionic species. Formally the reaction of tungstate with acid can be written

$$Na_2W(OH)_8 + (p/6)HClO_4 = Na_{(12-p)/6}W(OH)_{(48-p)/6} + (p/6)NaClO_4 + (p/6)H_2O \quad (1)$$

In the system consisting of solvent, hydrolyzed isopolytungstate, and supporting electrolyte, the definition of isopolytungstate component species is, in accordance with Scatchard[7]

$$[Na_\nu W(OH)_{(48-p)/6}{}^{z'-} + z'Na^+ - (z'/2)(Na^+ClO_4^-)]_{N_{z'}} \quad (2)$$

where $z' = [(48 - p)/6] - \nu - 6$. Then the degree of aggregation, $N_{z'}$, is related to the turbidity due to the isopolytungstate, τ^*, by

$$1/N_{z'} = \frac{H''M'\Phi\psi'^2}{\tau^*} - \frac{z'^2M'}{2M_3} \quad (3)$$

where $H'' = 32000\pi^3n^2/3N\lambda^4$. Φ is the volume fraction of the solvent, N is Avogadro's number, n is the refractive index of the solution, and λ is the wave length of light used. M' is the molarity of the tungstate, $N_{z'}$ times the molarity of the polymeric component (2).

Unhydrolyzed Sodium Tungstate.—For $p = 0$, we have simple Na_2WO_4. Such a series was run in 2 *M* $NaClO_4$ supporting electrolyte. The values of Φ, calculated from density data, varied from 0.88 at 0.50 *M* WO_4^{2-} to 0.90 at 0.05 *M* WO_4^{2-}. The value of $\partial n/\partial M'$ for Na_2WO_4 was found to be 0.0300 l./mole. Recall that $\psi' = \partial n/\partial M' - (z'/2)\partial n/\partial M_3$ and $M_3 = 1.000$ (or 2.000) $+ (z'/2)M'$.[6] Using z' as a parameter, with obvious limits of 0 and 2, plots of $1/N_{z'}$ are shown in Figure 1. The degree of aggregation is the expected

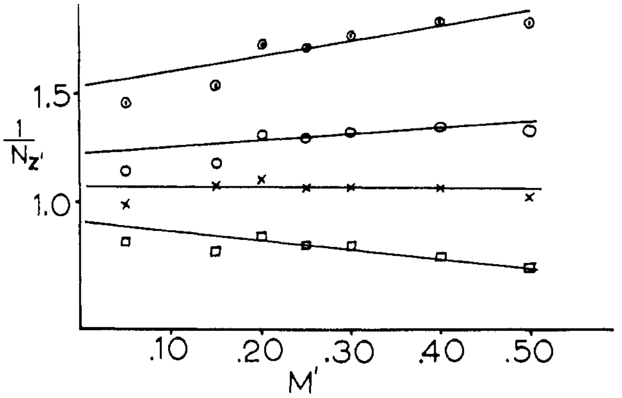

Figure 1.—$1/N_{z'}$ *vs.* M' for $p = 0$ series at 25°: ⊙, $z' = 0$; O $z' = 1.0$; ×, $z' = 1.5$; □, $z' = 2.0$.

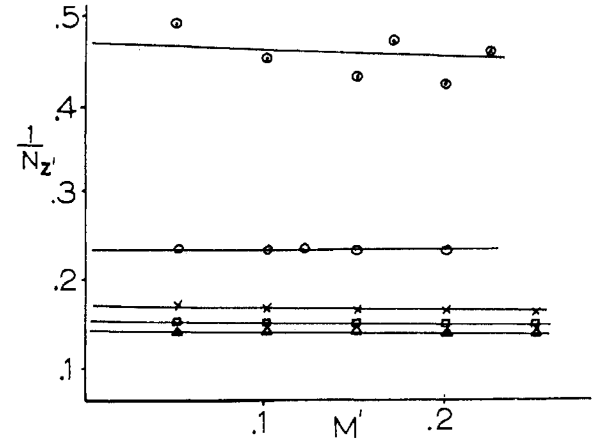

Figure 2.—$1/N_{z'}$ *vs.* M' with $z' = 0$, at 25°: ⊙, $p = 2$; O, $p = 4$; ×, $p = 6$; □, $p = 6.5$; △, $p = 6.75$.

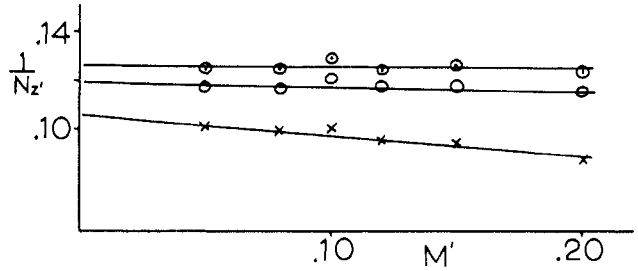

Figure 3.—$1/N_{z'}$ *vs.* M' for $p = 7$ series at 25°: ⊙, $z' = 0$; O, $z' = 0.2$; ×, $z' = 0.6$.

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[6] R. S. Tobias and S. Y. Tyree, Jr., *J. Am. Chem. Soc.*, **82**, 3244 (1960).

[7] G. Scatchard, *ibid.*, **68**, 2315 (1946).

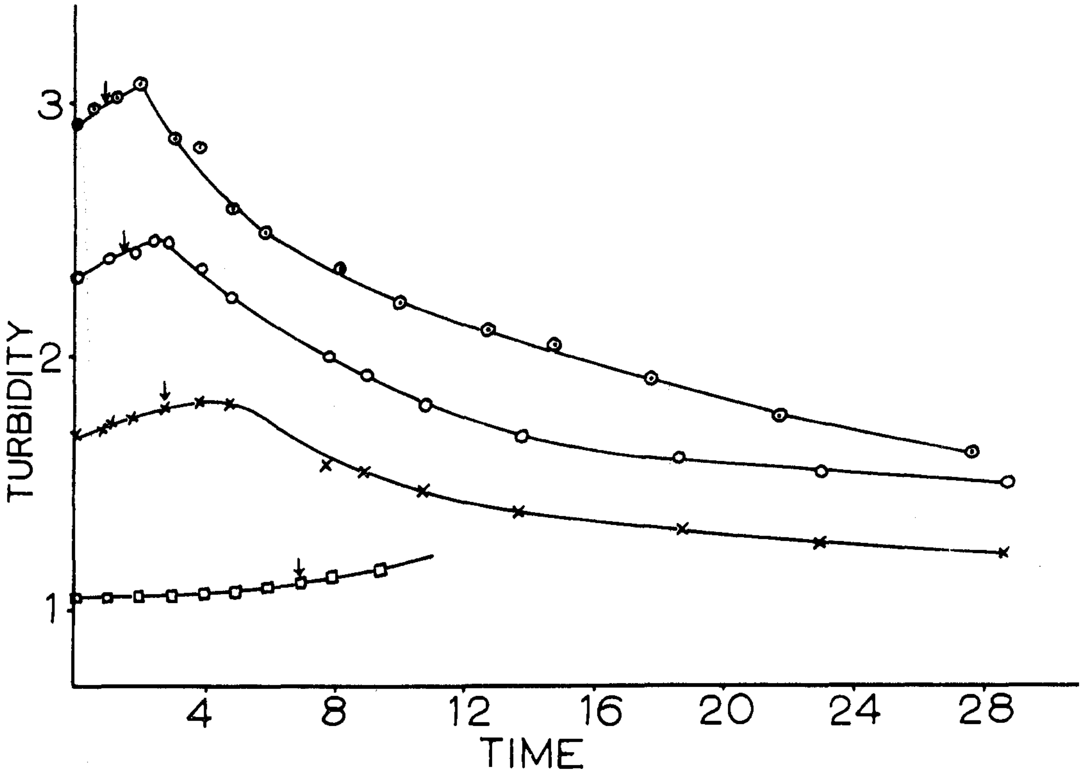

Figure 4.—Turbidity (arbitrary scale) *vs.* time in days for selected solutions, each at 25°; → indicates time at which crystals first appeared: ⊙, soln. 2.27; O, soln. 2.157; ×, soln. 2.17; □, soln. 1.057.

value of 1 at a z' value of 1.5, not unreasonable in 2 *M* $NaClO_4$, and the slope of the plot is most nearly zero for the same value of z'. Such solutions are stable indefinitely in our experience.

Sodium Tungstate, with $2 < p < 8$.—For solutions with p = 2–7 crystals were observed to separate from most of the 2 *M* $NaClO_4$ solutions in time. Only for solutions less than 0.02 *M* in W(VI) and at very low p did no crystallization take place during the months of observation. Also from 1 *M* $NaClO_4$ solutions, crystallization occurred in time from solutions 0.03 *M* in W(VI) or greater. The crystals in all cases appeared to be the same. Selected samples of crystals from different solutions gave similar chemical analyses. In addition, the powder patterns of several selected batches were the same and could be indexed in accord with Parrish and Irwin[8] as sodium paratungstate. We conclude that all crystals obtained in our experiments were paratungstate. In general for a given value of p the more concentrated the W(VI) the sooner the crystallization started. However, only in the most concentrated solutions, 0.3–0.5 *M* in W(VI), and at high p values, did crystallization start during the day on which the solutions were prepared. Usually the crystallization continued over a period of many weeks. Measurements of pH on solution 2.157 were made for 34 days while it was crystallizing. No change was detected. From this it can be concluded that no further protonation is involved in the crystallization process. The several values of $\partial n/\partial M'$ are 0.0293, 0.0279, 0.0264, 0.0263, 0.0261, and 0.0264 for p = 2, 4, 6, 6.5, 6.75, and 7, respectively. Plots of $1/N_{z'}$ for the several series are shown in Figures 2 and 3. All plots in Figure 2 are for $z' = 0$. In Figure 3, z' is varied as the parameter for the $p = 7$ case. The results for the latter case are in essential agreement with those of Aveston.[3] It is tempting to estimate the equilibrium constant for the formation of the isopolyanion from the monomer from the plots of Figure 2. However, it must be recalled that none of these solutions was at equilibrium, each ultimately depositing crystals of paratungstate. The values of turbidity used to calculate $1/N_{z'}$ points in Figures 2 and 3 are those observed just after solution preparation. Variations of turbidity with time are shown for some $p = 7$ solutions in Figure 4.

There is an initial increase in turbidity which varies with concentration in the time required to reach a maximum value. There follows a decrease as crystallization removes solute from solution. The fact that crystals are observed before the maximum turbidity is reached may be a significant point. Turbidities of several solutions of sodium paratungstate in pure water were measured over lengthy time intervals. The results are shown in Figure 5. Again it is obvious that reactions among solute species are continuing over many hours. No consistency is to be found in the behavior of these latter solutions, one of the 0.05 *M* W(VI) solutions fluctuating in turbidity over twice the range of the 0.10 *M* W(VI) solutions. In this case the peak value of τ^* is approximately three times the value taken from solution 2.057 to calculate one of the points in Figure 3. It seems likely that solute species more highly aggre-

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[8] W. Parrish and B. W. Irwin, "Data for X-Ray Analysis," Vol. 1, Philips Technical Library, 1953.

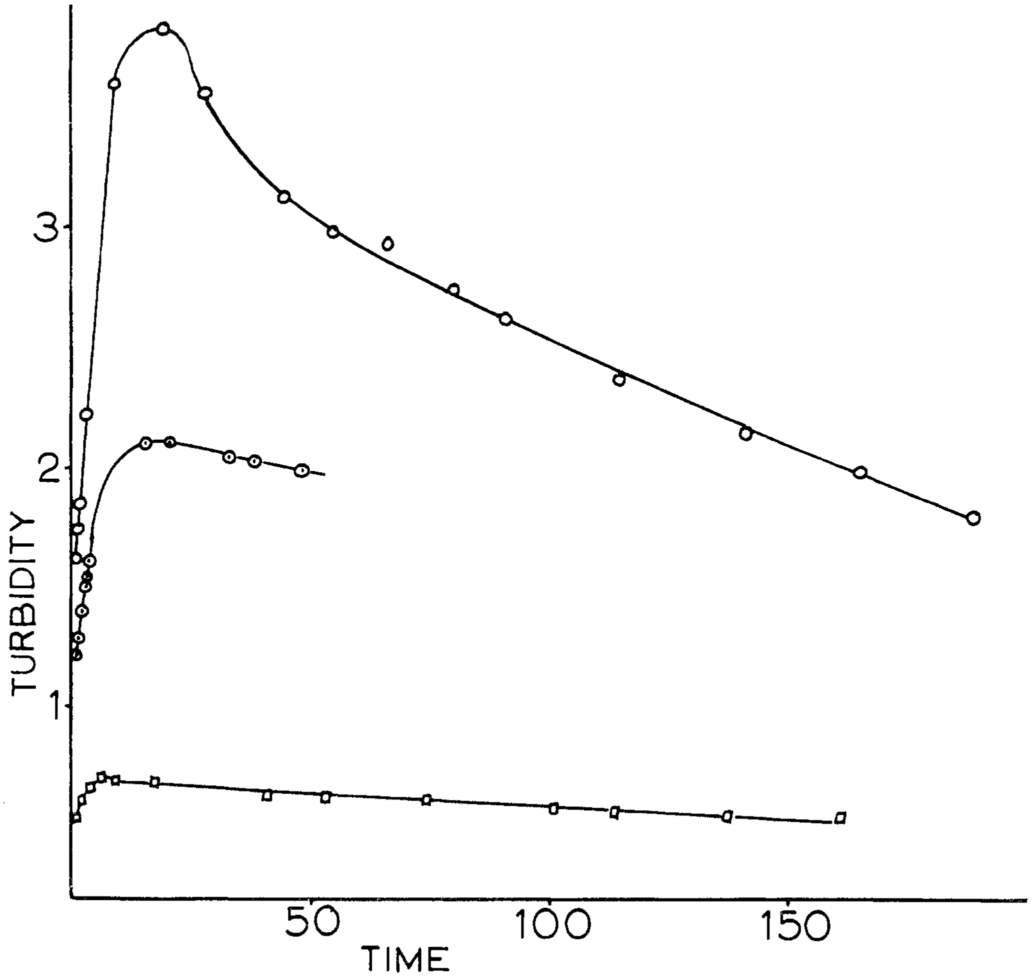

Figure 5.—Turbidity (arbitrary scale) *vs.* time in hours for paratungstate solutions, no supporting electrolyte, each at 25°: ⊙, 0.10 *M* W(VI); ○, 0.05 *M* W(VI); □, 0.05 *M* W(VI).

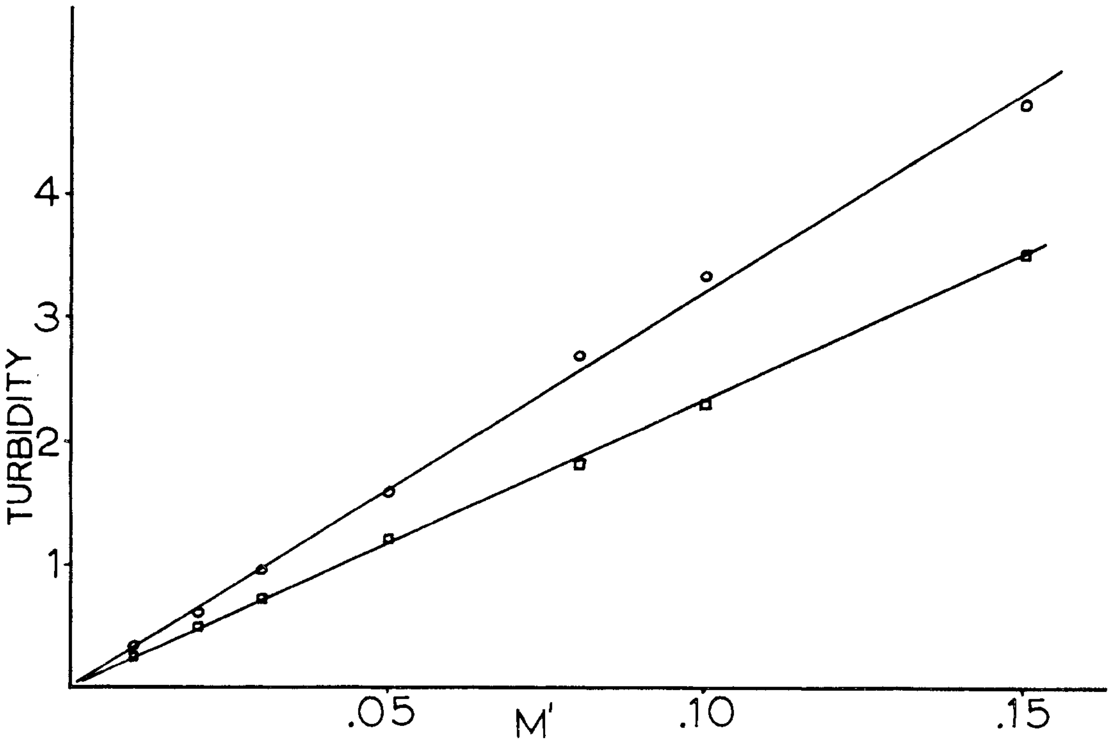

Figure 6.—$\tau^* \times 10^{-4}$ in cm.$^{-1}$ *vs.* M' for $p = 9$ series: ○, 25° solutions; □, solutions which have been heated to 50°.

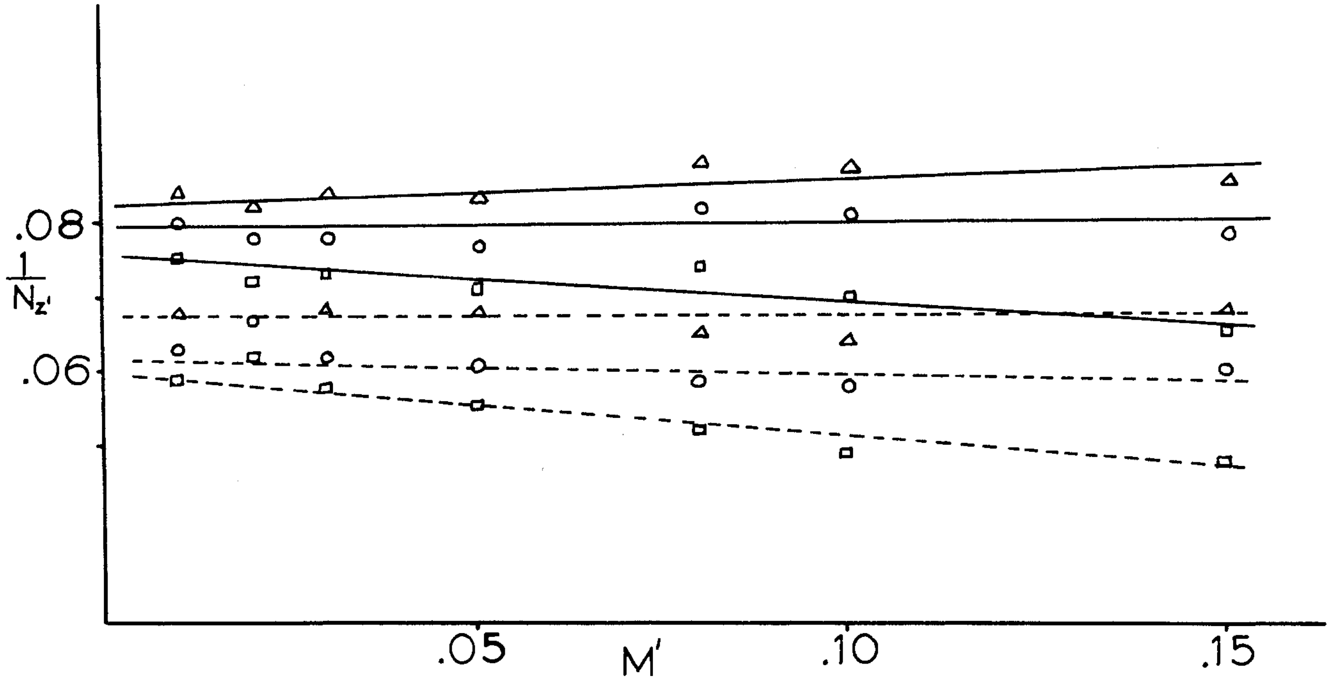

Figure 7.—$1/N_{z'}$ *vs.* M' for $p = 9$ series: △, $z' = 0$; ○, $z' = 0.2$; □, $z' = 0.4$; ———, after heating to 50°; ---------, 25° solutions.

gated than the dodecamer may be important intermediates in the approach to equilibrium. We conclude that we have not yet been able at room temperature to prepare solutions of isopolytungstate at $p = 7$ which can be shown to be at even a steady state, let alone at true thermodynamic equilibrium.

It is to be noted that the allowed variations in z' decrease as p increases. A concomitant result is smaller variations of the intercept, $1/N_{z'}$, with the parameter z'; compare Figures 1 and 3.

Sodium Tungstate at $p = 9$.—As $HClO_4$ is added to Na_2WO_4 solutions up to $p \sim 7$–8, a *temporary* white precipitate forms around the location where the drops of acid enter the solution. As more acid is added and $p = 8$ is passed, no further white precipitate is observed to form. In the $p = 9$ series, after all room temperature data were collected, each solution was thermostated at 50° for 6 days and brought back to room temperature. Refractive indices and turbidities were remeasured. It should be noted that the original room temperature data were taken immediately after preparation and did not vary over a 10-day period.

The value of $\partial n/\partial M'$ changed from 0.0284 to 0.0278 as a result of the heating procedure. The corresponding changes in turbidity values are shown in Figure 6. Plots of $1/N_{z'}$ for the two sets of measurements are shown in Figure 7. Essential agreement with Aveston on the degree of aggregation of 12 is obtained only after the solutions are heated. Once these solutions have been heated and returned to room temperature, no crystallization or changes in turbidity are observed on very long standing. We conclude that larger solute species must be important and long-lived intermediates in the aggregation process.

One solution at $p = 9$ was prepared by the method of Souchay,[9] using acetic acid and sodium acetate buffer in place of perchloric acid, still carrying out the solution preparation at room temperature. Both the refractive index increment value and the turbidity value due to the tungsten-containing solute agreed with the values obtained for the corresponding *heated* solution of the regular series. From this we believe that local high concentrations of strong acid are necessary for the formation of the larger, unstable solute species.

Sodium Tungstate at $p > 9$.—To date it has not been possible to obtain reproducible turbidity data on these series. The fluctuations in turbidity values for individual solutions are large and usually no acceptable data can be obtained after 2–3 days since the precipitates separating from the solutions cling to the sides of the scattering cells in sharp contrast to the paratungstate crystals, which fall to the bottom of the cells.

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[9] P. Souchay, *Ann. chim.* (Paris), **18**, 61, 73, 169 (1943).