Studies of the Tungsten-containing Species Present in Acidified Sodium Tungstate Solutions[1]

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Rayleigh turbidities and differential indices of refraction were measured and weight average ionic weights were calculated for sodium tungstate solutions acidified with perchloric acid. Aggregation or polymerization of the tungstate species as the solution is acidified is verified by this technique. Although the degree of polymerization does not change suddenly at certain H^+/WO_4^{2-} ratios, the change in degree of polymerization is not so uniform as to exclude the possibility of predominant species at certain H^+/WO_4^{2-} ratios. Some evidence for an intermediate predominant species between the monomer and hexamer is cited. Definite evidence is obtained for continued polymerization beyond the hexamer toward a possible dodecamer. The extent of polymerization beyond the hexamer is dependent both on H^+/WO_4^{2-} ratio and total tungsten concentration. It appears to be possible to use the light scattering technique to study the rate of polymerization of freshly prepared tungstic acid up to the point where precipitation commences.

Introduction

In order to elucidate the isopolytungstate system measurements of diffusion[3] and dialysis[4,5,6] coefficients of solutions containing the polyanionic species have been carried out. Polytungstate solutions have been studied by the use of spectrophotometric,[3,7-9] conductometric,[7,9,10] cryoscopic,[11,12] isopiestic[13] and pH[9,14] measurements. Thermometric,[7] conductometric,[7-9,15] and potentiometric[6,8,9,11,15,16] titrations have been employed in studies of these solutions. Self-diffusion[17] studies have been made over a limited range of concentrations.

It may be regarded as certain from the forementioned studies that as acid is added to a solution of $Na_2WO_4 \cdot 2H_2O$ polymerization of the monotungstate ion commences. The first very predominant species is the hexatungstate although, as Jander predicted and Anderson's, Biehler's and Pan and Hseu's data indicate there is reason to believe an intermediate predominant species may exist between the monotungstate and the hexatungstate. According to Jander depending on the concentration of the tungstate solution and the hydrogen ion concentration an equilibrium either between $HW_6O_{21}^{5-}$ and $H_3W_6O_{21}^{3-}$ or between $HW_6O_{21}^{5-}$ and a dodecatungstate apparently exists.

The question arises as to whether there are rather sharp lines of demarcation between the point where a given species is predominant and another species is predominant or whether there are no predominant species at any time. Also if predominant species exist the question arises as to what factors cause a change in the species predominant at a given time. Jander[4] has set ranges of pH and concentration in which he believes a given species to be very predominant.

This paper deals with the application of the light scattering and related techniques to a study of sodium tungstate solutions of several concentrations to which various amounts of perchloric acid are added. If polymerization of monotungstate does take place with increase in hydrogen ion concentration it should prove possible to follow the change in weight average ionic weight of the isopolytungstate species with change in H^+/WO_4^{2-} ratio. Likewise some indication as to the effect of tungstate concentration on the degree of polymerization at a given H^+/WO_4^{2-} ratio may be available from these studies.

Experimental

Instruments.—A standard Phoenix Precision Instrument Company differential refractometer designed according to Brice[18] was used to obtain differences between the refractive indices of the solution and solvent as the concentration of the solution was varied. This instrument was standardized using standard sucrose solutions and light of wave length 589 mμ from a sodium lamp source.

Turbidity measurements were made using a light scattering photometer fabricated in this Laboratory, similar in design to that described by Brice,[19] and calibrated using purified thiophene-free benzene, the absolute turbidity of which is given by the National Bureau of Standards[20] as 46×10^{-6} cm.$^{-1}$. Carbon tetrachloride, as would be expected if the instrument were functioning correctly, showed no dissymmetry.

Since the light scattering photometer was standardized using benzene and employed for aqueous solutions the usual correction was applied to account for the difference between the refractive index of benzene and that of water.[21,22]

A Leeds and Northrup line operated pH meter was used for potentiometric titrations, while a Beckman Model G pH meter was used to determine the pH of the polytungstate solutions. The meters were standardized against known buffer solutions.

Chemicals.—The chemicals were C.P. or reagent grade except for the sodium tungstate which in addition to being reagent grade met the specifications according to Dr. Folin.[23]

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(3) G. Jander and H. Schulz, Z. anorg. allgem. Chem., 162, 141 (1927).

(4) G. Jander and F. Exner, Z. physik. Chem., 190A, 195 (1941).

(5) G. Jander, ibid., 187A, 149 (1940).

(6) H. Brintzinger and C. Ratanarat, Z. anorg. allgem. Chem., 224, 97 (1935).

(7) G. Jander and W. Heukeshoven, ibid., 187, 60 (1930).

(8) G. Jander and U. Kruerke, ibid., 265, 244 (1951).

(9) E. Buchholz, ibid., 244, 149, 168 (1940).

(10) K. Pan, S. F. Lin and S. T. Sheng, Bull. Chem. Soc. Japan, 26, 131 (1953).

(11) P. Souchay, Ann. chim. (Paris), [11] 18, 61, 73, 169 (1943).

(12) G. Biehler, ibid., [12], 2, 489 (1947).

(13) R. Robinson and D. Sinclair, J. Chem. Soc., 642 (1934).

(14) H. T. S. Britton, ibid., 147 (1927).

(15) K. Pan and T. M. Hseu, Bull. Chem. Soc. Japan, 26, 126 (1953).

(16) H. T. S. Britton and W. L. German, J. Chem. Soc., 1249 (1930).

(17) J. Anderson and K. Saddington, ibid., S381 (1949).

(18) B. A. Brice and M. Halwer, J. Opt. Soc. Am., 41, 1033 (1951).

(19) B. A. Brice, M. Halwer and R. Speiser, ibid., 40, 768 (1950).

(20) L. M. Kushner, ibid., 44, 155 (1954).

(21) C. I. Carr, Thesis, Univ. Calif., 1949.

(22) J. T. Edsall, H. Edelhoch, R. Lontie and P. R. Morrison, THIS JOURNAL, 72, 4641 (1950).

(23) O. Folin, J. Biol. Chem., 106, No. 1, 311 (1934).

Results and Calculations

Debye[24,25] has derived the expression for the turbidity of dilute solutions. It can be expressed as

$$\tau = \frac{32\pi^3 M c n_0^2}{3\lambda^4 N}\left(\frac{n - n_0}{c}\right)^2 \qquad (1)$$

where M equals the weight average ionic or molecular weight of the solute. Let

$$H = \frac{32\pi^3 n_0^2}{3\lambda^4 N}\left(\frac{\Delta n}{\Delta c}\right)^2 \qquad (2)$$

Then

$$\tau = HMc \text{ or } Hc/\tau = 1/M \qquad (3)$$

Equation 3 is for ideal solutions. The addition of the term $2Bc/RT$, where B is an empirical constant which expresses the interaction between the solvent and the individual segments of dissolved polymer molecules, gives an equation for non-ideal solutions.

$$Hc/\tau = 1/M + 2Bc/RT \text{ or } c/\tau = 1/MH + 2Bc/RTH \qquad (4)$$

If c/τ is plotted against c and a straight line is drawn through the points and extrapolated to zero concentration then the intercept represents the value of c/τ at infinite dilution and is equal to $1/MH$ or in other words

$$(c/\tau)_{c=0} = 1/MH \text{ or } M = 1/H\,(c/\tau)_{c=0} \qquad (5)$$

Thus by plotting two graphs (1) Δn versus c in order to obtain the slope and thus $\Delta n/\Delta c$ so that H can be calculated and (2) c/τ versus c and extrapolate to $c = 0$ to obtain $(c/\tau)_{c=0}$ it is possible to calculate M, the weight average molecular or ionic weight of the solute.

Δn for a given sodium tungstate solution to which a certain amount of perchloric acid has been added is corrected by subtracting a Δn for the sodium perchlorate formed assuming complete consumption of the acid to form sodium perchlorate. The corrected Δn is divided by the appropriate Δc expressed in g./cc. and the value is squared to obtain $(\Delta n/\Delta c)^2$ which is used in the equation for M.

The τ value used in the equation for M is obtained from the τ value for the solution, determined experimentally for a given sodium tungstate solution to which a certain amount of perchloric acid is added, by subtracting a τ value for the sodium perchlorate formed assuming complete conversion of acid to salt. The tungstate concentration expressed in g./cc. is divided by the corresponding corrected τ value to obtain c/τ for a given concentration and H^+/WO_4^{2-} ratio. c/τ values are obtained for concentrations ranging from 0.5 to 0.025 molar in sodium tungstate and 1/2 to 3/2 H^+/WO_4^{2-} ratio. For a given H^+/WO_4^{2-} ratio these values are plotted against c in g./cc. A straight line is drawn through the points and extrapolated to zero concentration to obtain $(c/\tau)_{c=0}$ needed in the equation for M.

The assumption as to what constitutes the solute is important. The two extreme cases would be (1) to calculate c/τ as if the solute were WO_4^{2-} neglecting the excess Na^+ over and above that accounted

for in the $NaClO_4$ or (2) to calculate c/τ as if the solute were Na_2WO_4 neglecting the Na^+ accounted for in the $NaClO_4$. The true value of the solute is somewhere between these extremes. In all cases the H^+ is neglected. This is justified since in many cases the solutions are approximately neutral. In those cases where the H^+/WO_4^{2-} ratio is 7/6 or more and the pH of the solution is in the acid region the hydrogen ion concentration is still negligibly small as compared to the tungstate ion and sodium ion concentrations. Any hydration of the tungstate ion is neglected as being too uncertain to incorporate in these calculations.

Determinations of the weight average ionic weight of Na_2WO_4 in solution and the weight average molecular weight of raffinose in solution were made to check the sensitivity and resolution of the photometer. These proved quite satisfactory as indicated in Table II.

TABLE I

SAMPLE DATA FOR SOLUTIONS WITH H^+/WO_4^{2-} RATIO 3/2

Concn. of Na_2WO_4, g./cc.	Concn. of WO_4^{2-}, g./cc.	Na_2WO_4 $c/\tau \times 10^{-2}$	WO_4^{2-} $c/\tau \times 10^{-2}$
0.1470	0.1240	0.6691	0.5644
.1176	.0992	.8134	.6872
.0882	.0744	.9476	.8009
.0735	.0620	1.0135	.8570
.0588	.0496	1.0877	.9146
.0294	.0248	1.2030	1.0135
.0074	.0062	1.3102	1.0877

	H	$(c/\tau)_{c=0}$
For Na_2WO_4 as solute	2.61×10^{-6}	1.360×10^2
For WO_4^{2-} as solute	3.69×10^{-6}	1.137×10^2

Sample calculation

$M = 1/H(c/\tau)_{c=0}$ according to eq. 5
$M = 1/(2.61 \times 10^{-6})(1.36 \times 10^2)$
$M = 2820$

TABLE II

WEIGHT AVERAGE IONIC WEIGHT OF TUNGSTEN-CONTAINING SPECIES[a]

H^+/WO_4^{2-} ratio	Na_2WO_4 for solute	WO_4^{2-} for solute	Theoretical
1/2	613	519	
2/3	839	709	$W_3O_{11}^{4-} = 728$
5/6	1026	860	
1/1	1254	1062	
7/6	1684	1405	$HW_6O_{21}^{5-} = 1441$
4/3	2073	1723	
3/2	2820	2380	$W_{12}O_{40}^{8-} = 2848$
Na_2WO_4		271	$WO_4^{2-} = 248$

[a] The weight average molecular weight for raffinose was found to be 584. The theoretical value for hydrated raffinose is 594 and for anhydrous raffinose is 504.

Table I contains sample data and sample calculations for solutions with H^+/WO_4^{2-} ratio 3/2. Table II shows the weight average ionic weight for the solute at the various H^+/WO_4^{2-} ratios studied.

Discussion

The data given in Table II verify the fact that aggregation or polymerization of the tungstate species takes place as the solutions are acidified. Note the agreement between the observed values at the 2/3 and 7/6 ratios and the theoretical values for a trimer and a hexamer, respectively.

(24) P. Debye, *J. Appl. Phys.*, **15**, 388 (1944).
(25) P. Debye, *J. Phys. Chem.*, **51**, 18 (1947).

Figure 1 is a plot of τ, turbidity, *versus* H^+/WO_4^{2-} ratio. The rate of increase of τ increases above the 7/6 ratio in all cases. This increase is more striking the greater the total tungsten con-
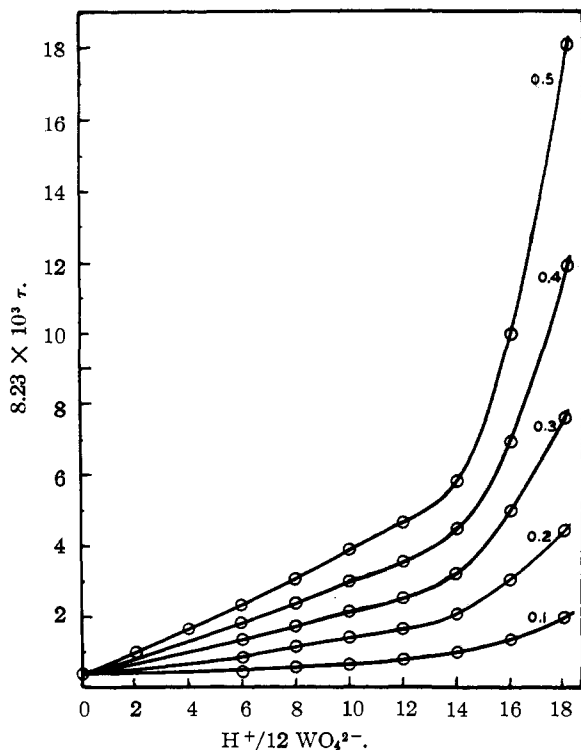

Fig. 1.—Turbidity, τ, as a function of H^+/WO_4^{2-} ratio for solutions 0.1, 0.2, 0.3, 0.4 and 0.5 M in sodium tungstate.

centration. It would seem from these observations that an equilibrium exists between the tungsten-containing species (hexamer) found at a H^+/WO_4^{2-} ratio of 7/6 and a larger species, possibly the dodecamer, such that this larger species becomes increasingly more predominant not only as the 3/2 ratio is approached but also as the total tungsten concentration is increased. In other words, for a given ratio above 7/6 the more concentrated the solution the more predominant the larger species.

Figure 2 is a plot of Δn, the difference between the index of refraction of the solution and solvent, *versus* H^+/WO_4^{2-} ratio for a solution 0.5 M in tungstate. A theoretical Δn value was obtained for a given solution by adding together the Δn value for a tungstate solution of that concentration plus a Δn value for the perchloric acid used in that case, assuming no reaction between the tungstate and the perchloric acid. (It should be noted that indices of refraction of dissolved salts are additive if no reaction takes place.[1,26]) The observed Δn values for these solutions always fall below the theoretical values indicative of reaction at all H^+/WO_4^{2-} ratios. An inflection in the observed curve at the 7/6 ratio is indicative of a predominant species (hexamer) present at this ratio. The gradual inflection between H^+/WO_4^{2-} ratios 0 and 7/6 indicates the possibility of an intermediate pre-

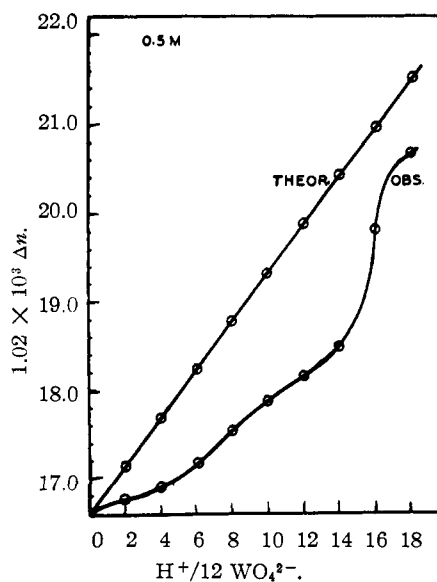(26) T. G. Berg, Z. anorg. allgem. Chem., **273**, 291 (1953).

Fig. 2.—Δn as a function of H^+/WO_4^{2-} ratio for a solution 0.5 M in sodium tungstate.

dominant species between the monomer and the hexamer.

Figure 3 is a differential curve of the data plotted in Fig. 2. Here $\Delta(\Delta n)$, the difference between the observed Δn and theoretical Δn is plotted *versus* H^+/WO_4^{2-} ratio for a solution 0.5 M in tungstate. The sharp break at H^+/WO_4^{2-} ratio
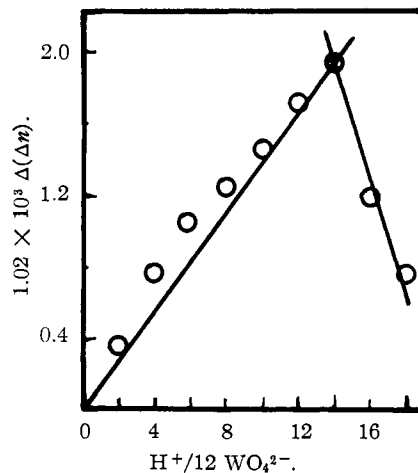

Fig. 3.—A differential curve of the data plotted in Fig. 2.

of 7/6 is indicative of the predominance of the hexamer at this ratio. If no intermediate species existed between the monomer and hexamer one would expect the points on the $\Delta(\Delta n)$ *versus* ratio curve between the 0 and 7/6 ratio to fall on the straight line drawn between these points. As is shown in Fig. 3 the observed points do not fall on the expected line but rather veer away from the expected line and then about half way between the 0 and 7/6 ratio turn back toward the expected line. This could be interpreted to be indicative of an intermediate about half way between the 0 and 7/6 ratio. In support of this idea note again the fact that the observed weight average ionic weight at the
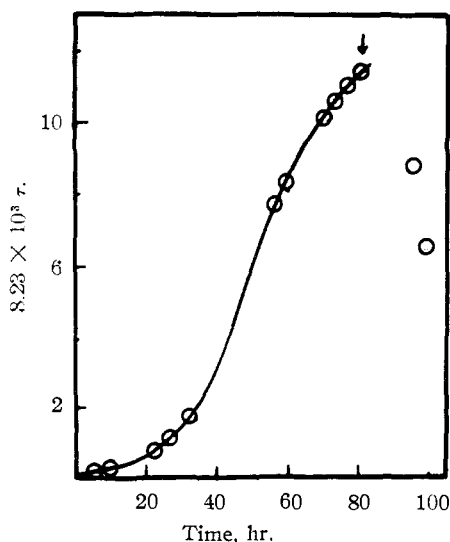
Fig. 4.—Turbidity, τ, as a function of time for a solution 0.025 M in sodium tungstate and having a $H^+/WO_4{}^{2-}$ ratio of 2 to 1. The arrow indicates the point when cloudiness was first noted in the solution.

2/3 ratio agreed remarkably well with the theoretical value for a trimer. This indication of an intermediate between the monomer and the hexa-

mer is most evident in the solutions of high total tungsten concentration.

On treating a tungstate solution with sufficient acid to convert the Na_2WO_4 to tungstic acid precipitation takes place. If the total tungsten concentration is small enough the solution remains clear even after adding sufficient acid to convert the Na_2WO_4 to tungstic acid and precipitation ensues only after a period of time has lapsed. Introductory studies of solutions having a $H^+/WO_4{}^{2-}$ ratio of 2 to 1 or in other words sufficient acid to convert all the Na_2WO_4 to tungstic acid indicate that it is possible to use the light scattering technique to study the rate of polymerization of freshly prepared tungstic acid to the point where actual precipitation commences. Figure 4 is a plot of τ versus time for a solution 0.025 M in Na_2WO_4 and having a $H^+/WO_4{}^{2-}$ ratio of 2 to 1. The turbidity increase with time is indicative of increasing polymerization of the tungsten containing species as the solution ages. In Fig. 4 the arrow indicates the point where visible cloudiness was first noted in the solution. Beyond this point τ began to decrease and actual precipitation commenced. In the case of a solution 0.05 M in tungstate 24 hours passed before visible cloudiness was observed while with a 0.10 M solution cloudiness ensued immediately.

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Chemistry of Rhenium and Technetium. I. Synthesis of ReCl5, TcCl4 and Related Compounds

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A general method for the synthesis of anhydrous metal chlorides has been developed. It is a modification of the method of Michael and Murphy in which the metal oxide and carbon tetrachloride are heated to 400° in a sealed glass tube. The glass tube is contained in a metal bomb with carbon tetrachloride or water in it to equalize the pressure. Pure preparations of ReCl5, TcCl4, MoCl5, WCl6 and TaCl5 have been made. Preliminary results also indicate that Fe, Zr, Be and V oxides are completely converted to chlorides; that Zn, Al, La, Th and Nb oxides are partially converted; and that Co and Ni oxides are not converted. The highest chloride formed by the metal is found in all known cases. Technetium yields a blood-red powder identified by analysis as the tetrachloride. Thus, under ordinary conditions, the highest chloride of Tc is different from that of Re, which forms a pentachloride.

Introduction

The general methods of preparing anhydrous metal halides have been reviewed earlier.[2] The method of Michael and Murphy,[3] in which the metal oxide and carbon tetrachloride react in a sealed tube, has been modified to overcome the difficulty of frequent breaking of the glass tubes at higher temperatures. At the temperature required to bring about the complete conversion of some oxychlorides to the chlorides, high pressures are generated which must be balanced by an external pressure. The balancing pressure is supplied by placing the sealed tube inside a high-pressure steel reaction vessel with heater[4] containing the proper amount of

a liquid. Then the whole assembly is heated. If water is used as the external liquid, heavy wall tubes must be used, because although the pressure at the reaction temperature can be made equal inside and outside the glass tube, the pressure difference at intermediate temperatures is great enough to break standard wall tubing. If carbon tetrachloride is used outside, standard wall glass tubing can be used. In the latter case, however, corrosion of the containing steel vessel is more rapid, but not alarmingly so.

Experimental

Method.—The standard conditions used in this Laboratory are 8 cc. of liquid carbon tetrachloride at room temperature for every 26 cc. of volume in the glass reaction vessel. The amount of metal oxide is that calculated to have a fivefold excess of carbon tetrachloride present, according to the equation for the reaction; e.g., $Re_2O_7 + 7CCl_4 \rightarrow 2ReCl_5 + 7COCl_2 + 2Cl_2$. The excess CCl_4 is needed to dissolve and

(1) Bell Telephone Labs., Inc., Murray Hill, N. J.

(2) S. Y. Tyree, Jr., Inorg. Syntheses, 4, 104 (1953).

(3) A. Michael and A. Murphy, Am. Chem. J., 44, 365 (1910).

(4) Obtainable from the American Instrument Company, Silver Spring, Md.