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Study of Soluble Tungstate Species by Solvent Extraction

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Summary

Tungsten is extracted from acidic tungstate solutions by the long-chain tertiary alkyl amine, tri-*n*-caprylamine, in benzene. Distribution data derived from solvent extraction are interpreted in terms of the predominating tungsten species present in the aqueous phase. The results show that the nature of the tungstate species extracted by tri-*n*-caprylamine changes markedly with the pH of the system. Further, the order of extraction is consistent with the order in which tungstate species should form as a function of the ratio of acid equivalents to moles of tungstate ions in solution.

INTRODUCTION

The chemistry of tungsten in solution has been studied extensively by various techniques involving polarography (*1,2*), paper chromatography (*3,4*), light absorption (*5*), turbidity (*6*), molecular weight (*7,8*), ultracentrifugation and Raman spectroscopy (*9*), infrared spectroscopy (*10*), absorption spectroscopy (*11*), radiochemistry (*12,13*), and precipitation (*14*). Much of the reported work concerns the existence of tungstate species in acidified solutions with particular reference to the molar ratio of acid to tungstate, the tungsten content of various species, and the degree of aggregation or polymerization of soluble polytungstates. The present investigation is concerned with the application of solvent-extraction techniques to the study of soluble tungstate species.

The extraction of metals by amines has been investigated by various workers (*15–20*). Recent reviews on the solvent extraction of inorganic species (*21*) and on the extraction of metal ions from acid solution (*22*) contain many references to extraction by amines. In acid solutions, the amine is converted to a salt form which remains essentially undissociated in the hydrocarbon solvent. A generally accepted mechanism of extraction is one in which the amine functions as a liquid anion-exchanger. The simple acid anion of the amine salt in the organic phase is readily displaced by an anionic complex of the metal present in the aqueous phase.

Very little solvent-extraction data concerning tungsten are recorded in the literature. Laskorin and co-workers compared the extraction of molybdenum and tungsten, emphasizing the extractability of molybdenum (*23*). Petrov et al. investigated the extraction of tungsten and molybdenum with tri-*n*-butylphosphate from strong acid solutions with emphasis on the separation of molybdenum from tungsten (*24*). Data on the extractability of metals, including tungsten, with numerous and various amines have been reported by Ishimori et al. (*25*), Coleman (*26*), and Maeck et al (*27*).

The detailed study reported herein concerns the extraction of tungsten from acidified tungstate solutions using tri-*n*-caprylamine as the extractant. In the preceding article, extraction of sulfuric acid in the tri-*n*-caprylamine–benzene system was investigated in order to determine the amine salt formed with sulfuric acid (*28*). Extraction at various pH levels can be interpreted in terms of the predominating tungsten species present in solution.

EXPERIMENTAL

Materials

The radio isotope ^{181}W (half-life, 140 days) in hydrochloric and hydrofluoric acids was obtained from Nuclear Science and Engineering Corporation and used as a tracer.

Tri-*n*-caprylamine was obtained as a commercial grade of symmetrical tertiary amine from General Mills' Chemical Division (Alamine 336). The method for the purification of the amine is given in the preceding article (*28*).

The amine bisulfate, prepared under conditions which ensured the formation of the bisulfate, was used throughout the experiments.

All other chemicals used were reagent grade.

Procedures

The aqueous phase was prepared to contain a countable quantity of radioisotope ^{181}W, in a concentration of the order of 10^{-7} *M*. The organic phase contained varying amounts of the amine in bisulfate form. Equal volumes of the aqueous and organic phases were mixed in glass-stoppered volumetric flasks, shaken mechanically at 25 ± 0.5°C for 2 hr, and allowed to settle for 1 hr. Aliquots of both phases were removed and counted. Optimum equilibrium was determined from a plot of distribution coefficient versus shaking and settling times. The activity of ^{181}W was measured on a Baird Atomic Gamma-Ray Scintillation Well Detector and a 530 Gamma-Ray Spectrometer equipped with a 707 Automatic Sample Changer and a 610 Printer. The distribution coefficient was calculated as

$$K_d = \frac{\text{total W concentration in organic phase}}{\text{total W concentration in aqueous phase}} = \frac{\text{activity, organic}}{\text{activity, aqueous}}$$

The pH of the aqueous solutions was controlled by the usual buffering agents described by Clark and Lubs (*14,30*).

RESULTS AND DISCUSSION

A general expression for the liquid anion-exchange extraction of tungstate species by tertiary amine salts can be written with univalent anionic ligands as

$$n(R_3NHA)_{(org)} + [(W_xO_yH_z)^{n-}]_{(aq)} \rightleftharpoons [(R_3NH)_n{\cdot}W_xO_yH_z]_{(org)} + [n(A)^-]_{(aq)} \quad (1)$$

where (R_3NHA) and $(W_xO_yH_z)^{-n}$ represent the amine salt and the tungstate ion, respectively. The subscripts (aq) and (org) refer to the aqueous and organic phases, respectively.

The reaction involving the amine bisulfate is

$$\frac{n}{2}[(R_3NH{\cdot}HSO_4)_2]_{(org)} + [(W_xO_yH_z)^{n-}]_{(aq)} \rightleftharpoons [(R_3NH)_n{\cdot}W_xO_yH_z]_{(org)} + (nHSO_4^-)_{(aq)} \quad (2)$$

The corresponding mass-law expression, in terms of concentration rather than activity, is

$$K = \frac{[(R_3NH)_n \cdot W_xO_yH_z]_{(org)}([HSO_4^-]^n)_{(aq)}}{[[(R_3NH \cdot HSO_4)_2]^{n/2}]_{(org)}[(W_xO_yH_z)^{n-}]_{(aq)}} \tag{3}$$

If $(W_xO_yH_z)^{n-}$ is the predominant tungstate-ion species in the aqueous phase, then the ratio

$$\frac{[(R_3NH)_n \cdot W_xO_yH_z]_{(org)}}{[(W_xO_yH_z)^{n-}]_{(aq)}}$$

may be replaced by the distribution coefficient K_d to yield the following equation:

$$K_d \frac{([HSO_4^-]^n)_{(aq)}}{[[(R_3NH \cdot HSO_4)_2]^{n/2}]_{(org)}} \tag{4}$$

The expression which relates the distribution coefficient K_d (the ratio of tungsten in the organic phase to tungsten in the aqueous phase) to the corresponding mass-law expression K, in terms of concentration rather than activities, may be written as

$$K_d = K \frac{[[(R_3NH \cdot HSO_4)_2]^{n/2}]_{(org)}}{([HSO_4^-]^n)_{(aq)}} \tag{5}$$

As only a tracer level of tungsten is used, it can be assumed that the activity coefficients of the various species remain constant (*29*). A logarithmic plot of the distribution coefficient as a function of the amine salt concentration at a constant concentration of anionic ligand should yield a straight line. Further, the intercept of the straight line equals log K and the slope is equal to one-half of the charge on the tungstate anion being extracted (*16,19,20,31*). A typical plot of experimental data is shown in Fig. 1.

The most probable value of the charge on the extracted tungstate species was obtained by treatment of the data using the least-squares method, solving for log K and n in the equations

$$\sum_{i=1}^{k} \left[\log K + \frac{n}{2} \log[(R_3NH \cdot HSO_4)_2]_{(org)} - \log K_d\right] = 0 \tag{6}$$

$$\sum_{i=1}^{k} \left[\log K + \frac{n}{2} \log[(R_3NH \cdot HSO_4)_2]_{(org)} - \log K_d\right] [\log(R_3NH \cdot HSO_4)_2]_{(org)} = 0 \tag{7}$$

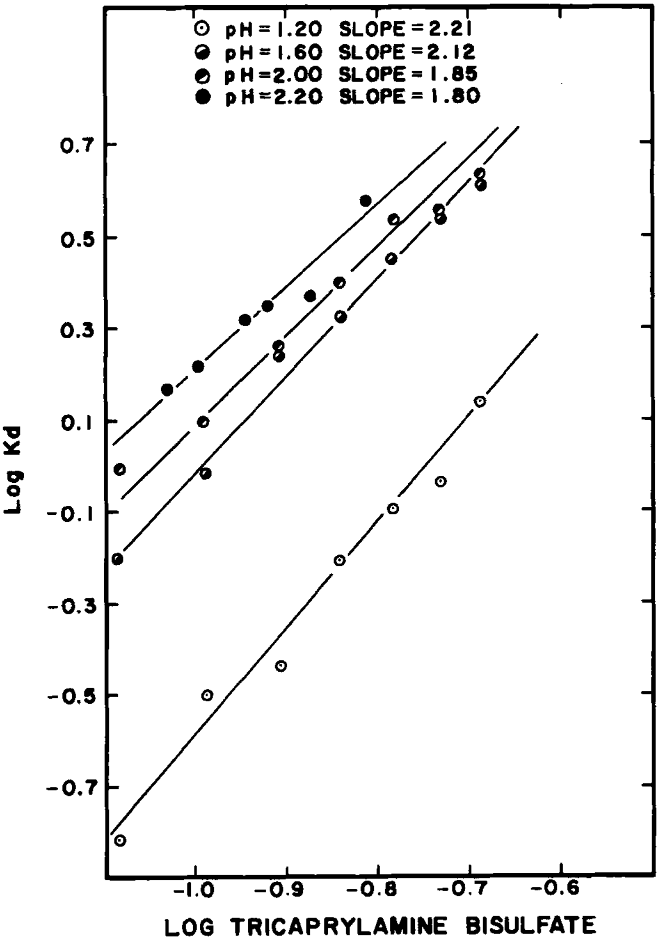

FIG. 1. Extraction of tungsten at various pH's as a function of tricaprylamine bisulfate in benzene.

Extraction data for tricaprylamine are summarized in Table 1. Figure 1 shows a plot, log K_d versus log concentration of amine bisulfate, for the data obtained over the pH range 1.2–2.2. In Fig. 2, the charge on the extracted tungstate species is plotted as a function of pH.

Many tungstate species have been proposed as existing in aque-

TABLE 1

Extraction of Tungsten as a Function of pH with Tricaprylamine (Alamine 336) Bisulfate in Benzene

pH	Slope from least squares	Slope from plot of log K_d vs. log conc. of alamine salt	Log K from least squares
1.20	2.27	2.22	1.68
1.60	2.12	2.05	2.03
1.80	2.26	2.30	2.41
2.00	1.69	1.85	1.81
2.20	1.80	1.70	2.10
2.40	3.37	3.20	2.91
2.60	3.39	3.37	2.88
2.80	3.78	3.60	3.54
3.00	3.30	3.60	2.72
3.40	3.12	3.06	2.61
4.00	3.44	3.40	2.85
4.20	5.18	5.03	4.82
4.40	4.52	5.00	4.32
4.60	4.34	4.26	4.31
5.00	4.67	4.77	4.24
5.40	10.37	10.60	9.59
5.60	10.10	10.50	8.60
5.90	10.72	11.40	9.41
6.00	10.62	10.00	9.15
6.20	1.03	1.00	1.95
6.40	0.77	0.90	1.67
6.60	1.28	1.00	2.16
6.80	0.72	1.00	1.91
7.00	0.74	1.00	1.63

ous solution, and the postulation of additional species does not appear warranted to explain our results. Instead, the pH regions over which certain species extracted are defined and a reasonably simple mechanism by which these species are formed is proposed.

Fortunately, it is well proven that the tungstate species in basic solution corresponds to the WO_4^{2-} tetrahedral ion (*1*,*5*). Freedman (*32*) suggested that the binding of protons by a doubly hydrated WO_4^{2-} ion weakens the tetrahedral complex and forms the octa-

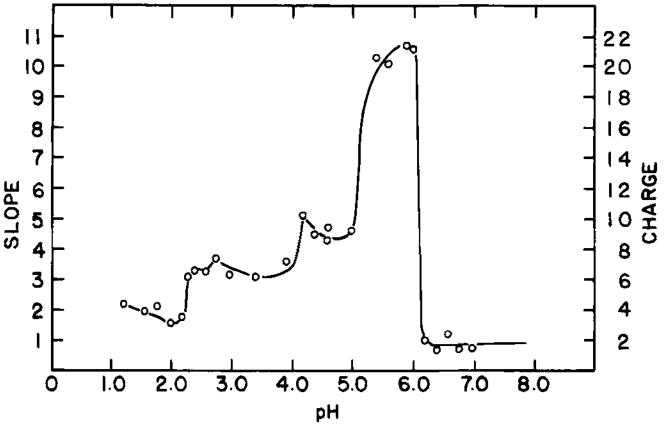

FIG. 2. Variation of charge on extracted tungstate species as a function of pH.

hedrally coordinated ion $H_4WO_6^{2-}$. The two differ only in configuration and not in degree of polymerization. The data of Table 1 and Fig. 2 confirm this model. The WO_4^{2-} or $H_4WO_6^{2-}$ species is extracted at pH values of 6.2 and above.

The existence of the usual WO_4^{2-} ion at high pH's having been established, there remains the question of which polytungstates are extracted in the acid region. Recent papers on polyanion equilibria (*3,4,33,34*) give excellent references to the earlier literature. The existence of the *p*-tungstate A ion, $HW_6O_{21}^{5-}$, and the pseudo-*m*-tungstate ion, $H_3W_6O_{21}^{3-}$, appears to be well established and corresponds to the addition of 7 and 9 equivalents of acid to 6 moles of the tungstate ion, WO_4^{2-}, respectively; i.e.,

$$7H_3O^+ + 6WO_4^{2-} = HW_6O_{21}^{5-} + 10H_2O$$

$$9H_3O^+ + 6WO_4^{2-} = H_3W_6O_{21}^{3-} + 12H_2O$$

The corresponding but more highly condensed species, namely, the *p*-tungstate ion, $W_{12}O_{46}^{20-}$, and the *m*-tungstate ion, $H_2W_{12}O_{40}^{6-}$, are found in the solid state (*14,35–37*). The presence of the *m*-tungstate ion, $H_2W_{12}O_{40}^{6-}$, in concentrated solutions has been claimed by Jander and Exner (*38,39*).

The more highly condensed *m*-tungstate, $H_2W_{12}O_{40}^{6-}$, and *p*-tungstate, $H_{10}W_{12}O_{46}^{10-}$, can be represented as forming from the same ratio of equivalents of acid to tungstate ion as their well-established solution equivalents, the pseudo-*m*-tungstate ion, $H_3W_6O_{21}^{3-}$, and the *p*-tungstate A ion, $HW_6O_{21}^{5-}$; i.e.,

$$14H_2O^+ + 12WO_4^{2-} = H_{10}W_{12}O_{46}^{10-} + 16H_2O$$

$$18H_3O^+ + 12WO_4^{2-} = H_2W_{12}O_{40}^{6-} + 26H_2O$$

It is therefore reasonable to think of these highly condensed ions, containing 12 tungsten atoms, as formed by the combination of two 6-tungsten-atom species; i.e.,

$$4H_2O + 2HW_6O_{21}^{5-} = H_{10}W_{12}O_{46}^{10-}$$

$$2H_3W_6O_{21}^{3-} = H_2W_{12}O_{40}^{6-} + 2H_2O$$

Bettinger and Tyree (*6*) found evidence for a trimer, $W_3O_{11}^{4-}$, using light-scattering techniques to determine average ionic weights. They noted that the extent of polymerization is dependent upon the H_3O^+/WO_4^{2-} ratio and the total tungsten concentration. The trimer was postulated to exist between the *o*-tungstate, WO_4^{2-}, and the *p*-tungstate A ion, $HW_6O_{21}^{5-}$. Evidence for polymerization beyond the hexamer to a dodecamer $W_{12}O_{40}^{8-}$ was also given. Freedman (*32*) postulated the existence of a limiting tritungstate ion, $H_4W_3O_{13}^{4-}$, from the slope of dilution curves and also from structural and geometric deductions. This trimer differs from $W_3O_{11}^{4-}$ only in that it has two bound waters. He suggested also that the *p*-tungstate ion be written as $H_{10}W_{12}O_{46}^{10-}$, basing his suggestion on the assignment of a hydrogen atom to each triply linked oxygen in Lindqvist's structure of the $W_{12}O_{46}^{20-}$ *p*-tungstate ion (*35*).

Other complex polytungstates have been proposed, but the basis for their postulation is less secure. Considering polytungstates as formed by the addition of acid to WO_4^{2-}, a general equation for the formation of polytungstates, without hydrogen, can be written:

$$aH_3O^+ + 12WO_4^{2-} = W_{12}O_{48-(a/2)}^{(24-a)} + \tfrac{3}{2}aH_2O$$

The polytungstates, $W_{12}O_{46}^{20-}$, $W_3O_{11}^{4-}$ ($W_{12}O_{44}^{16-}$), $W_{12}O_{41}^{10-}$, and $W_{12}O_{40}^{8-}$ are members of such a series, having as the end member tungstic acid, i.e., $WO_3 \cdot H_2O$. Table 2 shows all the species in order of increasing ratio of H_3O^+/WO_4^{2-}, including the proposed polytungstate species containing hydrogen.

TABLE 2

Polytungstates in Order of Increasing Ratio of H_3O^+/WO_4^{2-} Based on $12WO_4^{2-}$ Ions in the Equation: $aH_3O^+ + 12WO_4^{2-} = bW_xO_yH_z^{n-} + wH_2O$

a	b	Polytungstate	w
4	1	$W_{12}O_{46}^{20-}$	6
8	1	$W_3O_{11}^{4-}$	12
	4	$H_4W_3O_{13}^{4-}$	4
14	1	$H_{10}W_{12}O_{46}^{10-}$	16
	2	$HW_6O_{21}^{5-}$	20
16	1	$W_{12}O_{40}^{8-}$	24
18	1	$H_2W_{12}O_{40}^{6-}$	26
	2	$H_3W_6O_{21}^{3-}$	24
24	12	$WO_3 \cdot H_2O$	24

The data plotted in Fig. 2 can be interpreted in terms of the information contained in Table 2. Tungstic acid is insoluble and is not extracted. Therefore, the most acidic ion that can be extracted is the pseudo-*m*-tungstate ion, $H_3W_6O_{21}^{3-}$. There is a slightly decreasing charge over the pH range 1.2 to 2.0. It is suggested that the $H_3W_6O_{21}^{3-}$ ion is being extracted in this low pH range as well as an unknown species of slightly greater charge, with the charge on the latter species increasing with decreasing pH.

Between pH 2.0 and 2.4, the charge on the extracted species increases approximately twofold. This change is believed to be associated with the further condensation of the pseudo-*m*-tungstate ion, $H_3W_6O_{21}^{3-}$, to the *m*-tungstate ion, $H_2W_{12}O_{40}^{6-}$, or possibly $W_{12}O_{40}^{8-}$. The narrow pH range over which this polymerization occurs is surprising. The charge over the pH range 2.4 to 3.4 is consistent with the extraction of the 12-*m*-tungstate ion. Again, a slightly decreasing slope is observed in the pH plot. This is attributed to the gradual formation of the *p*-tungstate A ion, $HW_6O_{21}^{5-}$, as represented by the equations

$$2H_2O + H_3W_6O_{21}^{3-} = HW_6O_{21}^{5-} + 2H_3O^+$$

$$4H_2O + W_{12}O_{40}^{8-} = 2HW_6O_{21}^{5-} + 2H_3O^+$$

$$6H_2O + H_2W_{12}O_{40}^{6-} = 2HW_6O_{21}^{5-} + 4H_3O^+$$

Although the equilibrium is obviously dependent upon pH, more than one species can be present in solution at the same time, depending upon the equilibrium constants.

Above pH 3.4, the charge of the extracted ion again increased, rising sharply between pH 4.0 and 4.2, to a value of about 10. Referring to Table 2, this is attributed to the dimerization of the *p*-tungstate A ion to $H_{10}W_{12}O_{46}^{10-}$, the 12-*p*-tungstate ion. The decreasing slope beyond pH 4.2 is perhaps related to the formation of the tritungstate species $W_3O_{11}^{4-}$ or $H_4W_3O_{13}^{4-}$, which should occur in this pH range. This decreasing tendency is opposed by an opposite, increasing trend which rises sharply between $pH = 5.0$ and 5.4, indicating a species having a negative charge of about 20. This species can be associated with the $W_{12}O_{46}^{20-}$ ion. Finally, above pH 6.0, this ion is no longer stable and the well-established WO_4^{2-} ion is extracted.

It has been shown that the tungstate species extracted by the tertiary amine changes markedly with the pH of the system and further that the extracted species follow a regular trend, depending upon the ratio of H_3O^+/WO_4^{2-}. The regions of stability found agree quite well with those given by Duncan and Kepert (3), who found the *p*-tungstate A ion between 3.2 and 6.2 and the *m*-tungstate ion at lower pH's. It is also worth noting that Bettinger and Tyree (*6*) found the $W_3O_{11}^{4-}$ ion between WO_4^{2-} and $HW_6O_{21}^{5-}$. If the complex ion charges are averaged in order of their ratio, H_3O^+/WO_4^{2-}, the $W_3O_{11}^{4-}$ ion falls in that region.

The indicated presence of a $W_{12}O_{46}^{20-}$ ion can be explained by the close similarity between the R_3NH^+ ion and the NH_4^+ ion. It is generally agreed that the lowest possible hydrate of ammonium *p*-tungstate is the pentahydrate having the composition $(NH_4)_{10}W_{12}O_{41}\cdot 5H_2O$. Thermogravimetric analyses run in this laboratory have shown a continuous weight loss beyond the pentahydrate with no indication of the formation of an anhydrous salt or other stable species before WO_3 is formed. Thus it has been concluded here and by Freedman (32) that the *p*-tungstate might be better expressed as $(NH_4)_{10}H_{10}W_{12}O_{46}$.

In neutral solutions, replacement of the hydrogen ions with R_3NH^+ ions is a possibility, with subsequent extraction of $(R_3NH)_{20}W_{12}O_{46}$.

Furthermore, the extraction from solution of an anion having a negative charge of about 20 lends further credence to the *p*-tungstate ion proposed by Lindqvist, namely, $W_{12}O_{46}^{20-}$ or $H_2W_{12}O_{42}^{10-}$ (*40*).

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