

EXTRACTION OF TUNGSTEN WITH TRIALKYLAMINE – EFFECT OF pH

Jaroslav PROCHÁZKA^{1,*}, Aleš HEYBERGER², Jan HORÁČEK³, Eva VOLAUFOVÁ,
Jitka VOBORSKÁ and Eva MACHÁČKOVÁ⁴

*Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic,
165 02 Prague 6, Czech Republic; e-mail: ¹ prochazka@icpf.cas.cz, ² heyberger@icpf.cas.cz,
³ horacek@icpf.cas.cz, ⁴ machackovae@icpf.cas.cz*

Received January 25, 2001

Accepted June 18, 2001

Extraction equilibrium in the system aqueous solution of sodium tungstate–solution of trialkylamine in a mixed diluent was investigated. A tertiary amine with C₇–C₉ straight alkyl chains was dissolved in a mixture of tributyl phosphate and kerosene and presaturated with sulfuric acid to give normal trialkylamine sulfate. Extraction isotherms at 25 °C and at several constant values of equilibrium pH were measured in a broad range of aqueous tungstate concentrations. pH 2.0–6.0 was adjusted by addition of sulfuric acid during equilibration. The equilibrium tungstate and sulfate contents in both phases were determined. A typical tungstate isotherm exhibits a steep ascending part in the low concentration range, corresponding to the region of anion exchange, and a flat part in the high concentration range, where the acid content in the organic phase is virtually exhausted. The level of the flat part decreases with growing pH, corresponding to the increasing number of negative charges per tungsten atom in the tungstate polyanions extracted. At pH > 5, also the effect of hydrolysis of amine sulfate could be detected.

Keywords: Liquid–liquid extraction; Ion exchange; Equilibrium; Tungsten; Tungstates; Wolfram; pH effect.

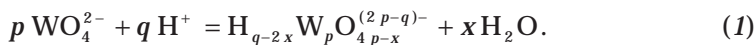
In modern processes of tungsten production from its ores and secondary raw materials, liquid extraction is used as an important purification step^{1–4}. Reactive extraction of tungstate anions from aqueous solution of sodium tungstates with high-molecular-weight aliphatic amines and re-extraction with aqueous ammonia are used to obtain high-purity ammonium dodecatungstate, (NH₄)₁₀(H₂W₁₂O₄₂)·4H₂O, an intermediate in production of metallic tungsten. In comparison with the earlier technologies using repeated precipitation and dissolution of calcium tungstate as the main purification step, the extraction reduces the costs and the amount of wastes.

Tertiary long-chain aliphatic amines were most frequently used as extraction agents in industrial tungsten separation and refining^{1–4}, but primary amines⁵ and quaternary ammonium bases⁶ were also investigated. The pro-

cess is strongly dependent on pH of the aqueous phase, high yields being achieved under weakly acidic conditions. For adjusting these conditions, the initial aqueous phase is acidified and the amines are pre-saturated with strong mineral acids, so that the process has a character of the exchange of tungstate anions with anions of the acid. The individual amines differ in the range of acidities of aqueous phase in which they can be applied. Whereas the quaternary ammonium salts can extract even at $\text{pH} > 8$, the salts of primary and tertiary amines undergo the hydrolysis at about $\text{pH} 6$. The lower limit of pH is set by the precipitation of "tungstic acid" at $\text{pH} < 2$.

The positive effect of increasing acidity of the aqueous phase on tungsten extraction is mainly due to the formation of various polyanions of tungsten with increasing number of tungsten atoms per negative charge^{4,7}. In the organic phase, these anions form amine complexes with higher number of tungsten atoms per amine, thus increasing the capacity of the extractant. They are also preferentially extracted from the aqueous phase⁶.

The process of transformation of tungstate anions into various polyanions by protonation can be described with the general equation



Here p is the degree of polymerization, q/p the degree of protonation, x/p the degree of dehydration and $y = (2p - q)/p$ the number of negative charges per tungsten atom. Kim *et al.*⁷ studied the process of protonation and polymerization at very low aqueous phase tungsten concentrations (10^{-7} mol/l) and interpreted their results by assuming the formation of various polyanions with decreasing pH ($\text{W}_{12}\text{O}_{46}^{20-}$; $\text{W}_3\text{O}_{11}^{4-}$; $\text{H}_4\text{W}_3\text{O}_{13}^{4-}$; $\text{H}_{10}\text{W}_{12}\text{O}_{46}^{10-}$; $\text{W}_{12}\text{O}_{40}^{8-}$; $\text{H}_2\text{W}_{12}\text{O}_{40}^{6-}$; $\text{H}_3\text{W}_6\text{O}_{21}^{3-}$). The influence of tungsten concentration on the formation of hexatungstate anions $\text{H}_3\text{W}_6\text{O}_{21}^{3-}$ was studied by Yatsimirskii and Romanov⁸ at $\text{pH} 2.6$ – 2.7 and 25°C . A significant enhancement of the polymer formation was detected at tungsten concentrations $> 1 \cdot 10^{-4}$ mol/l. In the review by Souchay *et al.*⁹ the dependence of some polymerization processes on time was described. Thus in fresh solutions, hexatungstate $\text{HW}_6\text{O}_{21}^{5-}$ predominates and transforms slowly into dodecatungstate $\text{W}_{13}\text{O}_{41}^{10-}$. Besides the acidity of aqueous phase, the overall concentration of W(VI) as well as the ionic strength and temperature of the solution affect significantly the relative content of individual polyanions. Baes and Mesmer¹⁰ presented a pH vs concentration diagram at constant ionic strength showing the areas of predominance of individual poly-

anions. Generally, a higher concentration favours the formation of polymers with a lower y value and a higher degree of polymerization.

Voldman and Zelikman presented a series of hexa- and dodecatungstates expected to form at increasing acidity in technological solutions of sodium tungstate (0.01–1 mol/l) in their review⁴. At pH 7.5–4, tungsten forms the anions $\text{HW}_6\text{O}_{21}^{5-}$, $\text{H}_2\text{W}_{12}\text{O}_{42}^{10-}$, $\text{H}[\text{H}_2\text{W}_{12}\text{O}_{42}]^{9-}$, $\text{H}_2[\text{H}_2\text{W}_{12}\text{O}_{42}]^{8-}$ and $\text{H}_3[\text{H}_2\text{W}_{12}\text{O}_{42}]^{7-}$ at pH 4–2 $\text{H}_2\text{W}_{12}\text{O}_{40}^{6-}$, $\text{H}[\text{H}_2\text{W}_{12}\text{O}_{40}]^{5-}$ and $\text{H}_2[\text{H}_2\text{W}_{12}\text{O}_{40}]^{4-}$.

In previous works^{6,7,11} and in industrial applications^{1–4}, high-molecular-weight trialkylamines were frequently used as tungsten extractants. Kerosene was usually applied as diluent, aromatics and high-molecular-weight alcohols were added to prevent the third phase formation. MacInnis and Kim¹² described the countercurrent experiments of tungsten extraction with trioctylamine dissolved in kerosene with tributyl phosphate as modifier. In most works, the amines were saturated with sulfuric acid and the exchange of tungsten anions for sulfate or hydrogensulfate anions was assumed to be the mechanism of formation of tungsten complexes with the amine. Addition of a neutral molecule of polytungstic acid to the amine complex with the same polyanion was also proposed¹³.

The measurements of tungsten extraction equilibrium were usually organized and presented as dependences of the distribution coefficient on pH at constant initial tungsten concentration. This form does not show separately the effects of equilibrium tungsten concentration in the aqueous phase and pH on tungsten extraction. Schrötterová and Nekovář^{5,13}, who studied the extraction of W(VI), Mo(VI) and Cr(VI) with the sulfate of primary amine Primene JMT, presented extraction isotherms as dependences of organic- vs aqueous-phase equilibrium tungsten concentrations at constant initial pH. The equilibrium pH values, also measured, increased with increasing tungsten concentration. At very low tungsten contents, the equilibrium pH was lower than the initial one. The latter effect was apparently due to partial stripping of the acid from the organic phase, the former to preferential extraction of tungsten ions with lower charge per tungsten atom.

The main aim of the present work was to investigate the extraction of tungsten with trialkylamine at constant pH of the aqueous phase. Trialkylamine sulfate was used as an extractant and a mixture of tributyl phosphate and kerosene as a diluent.

EXPERIMENTAL

System

The system examined consisted of aqueous sodium tungstate solution and of the organic phase containing trialkylamines (TAA) dissolved in a binary diluent. TAA were commercial products with C₇-C₉ straight alkyl chains (average molecular weight 363). The binary diluent was a mixture of kerosene (Chemopetrol, b.p. 135–200 °C) as inert diluent and tributyl phosphate (TBP) as modifier. Before use, TAA were washed with hydrochloric acid, sodium hydroxide and water. Other chemicals used were of chemical purity grade. The concentration of amines used was 0.1 and 0.5 mol/kg of diluent; the mass fraction of modifier in the diluent was 0.4. The initial organic phase was saturated with sulfuric acid to form the amine sulfate $\{(R_3NH)_4SO_4\}_o$. The initial aqueous phase was prepared by dissolving the dihydrate of sodium tungstate in distilled water. The range of initial tungsten concentration was 0.06–2.0 mol/kg H₂O.

Analytical Methods

Atomic absorption spectrometry was used for determination of tungsten in the aqueous phase (relative accuracy $\pm 4\%$). For determining W in the organic phase, the sample was re-extracted with aqueous sodium hydroxide and the re-extract was analysed. Sulfate anions in the aqueous phase were determined gravimetrically after removing tungsten (relative accuracy $\pm 3\%$). The sulfuric acid content in the organic phase was obtained from the re-extract by back-titration of the excess NaOH with 1 M hydrochloric acid. The accuracy of this measurement was about $\pm 5 \cdot 10^{-2}$ mol/l. The amine content in the organic phase was expressed in moles per kg of the diluent. Therefore, it was identical with the content before the saturation with sulfuric acid and could be determined by the titration with perchloric acid in acetic acid (relative accuracy $\pm 3\%$). After the saturation, the content of sulfuric acid was determined by titration with sodium methanolate (relative accuracy $\pm 5\%$). Water in the organic phase was determined using the Karl-Fischer method (relative accuracy $\pm 3\%$) and the results were used for calculating the concentrations in the anhydrous diluent.

Experimental Procedure

All experiments were carried out at 25 °C. In most experiments, the mass ratio of initial phases was unity. The ionic strength of the aqueous phase was not adjusted. The phases were brought in contact in a thermostatted mixing vessel. During the equilibration of phases, pH of the aqueous phase was measured and adjusted to the required value by addition of 4 M sulfuric acid; pH of the initial aqueous phase was not adjusted. The equilibrium pH range was 2.0–6.0. The acid was periodically added to the aqueous phase and pH was measured with a combined glass/AgCl electrode immersed in the water phase. The mixing intensity during the pH measurement and acidification was lowered to allow a partial separation of phases. In this way, the local over-acidification within the organic phase, leading to formation of an undesirable heavy third phase, was avoided. The whole procedure lasted about 1 h. After reaching the required value of pH (accuracy ± 0.1 pH units), the phases were kept in contact for about 2 h and mixed once more before final settling and separation to check for possible slow reactions in the system. No such effect was observed. Nevertheless, the reproducibility of the equilibrium measurements was significantly lower than that of the

analytical methods used. A slow process of crystal formation in the aqueous phase at pH > 4.5 is described below.

RESULTS AND DISCUSSION

Theoretical Considerations

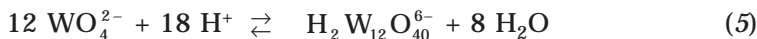
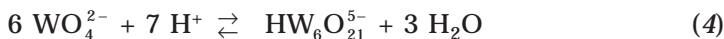
In the system considered, a number of chemical species exist and several simultaneous reactions take place. In the aqueous phase, there are polyanions of tungsten, sodium cations, sulfate and hydrogensulfate anions and protons. In the organic phase, there are various polytungstate complexes of amine, amine sulfate and free TAA. In the stoichiometric equations describing the process, the following main simplifying assumptions have been made: (i) In the initial organic phase, only the sulfate of TAA ($\{(R_3NH)_2SO_4\}_o$) is present. (ii) The polyanions in the amine complexes are identical with those present in the aqueous phase. With respect to a relatively short contact time, only the hexatungstate $HW_6O_{21}^{5-}$, and the dodecatungstate $H_2W_{12}O_{40}^{6-}$ are taken into account as representatives of the species with 0.83–0.5 negative charges per tungsten atom in pH and concentration ranges considered (pH 2.4–4.2; 0.06–2 mol/kg H_2O). (iii) The organic species dissolved in the aqueous phase are not taken into account.

The pertinent reactions are:

Dissociation of sulfuric acid:



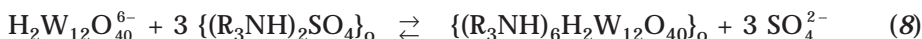
Protonation of tungstate anions:



Formation/decomposition of TAA sulfate:



Exchange of polytungstate and sulfate anions:



The subscript o denotes species in the organic phase.

Experimental Results

The first series of experiments was made at initial amine concentration in the organic phase $\{m_e^0\}_o = 0.1$ mol/kg diluent and at equilibrium pH 2.5, 3.5 and 4.5. In Fig. 1a, the results are shown in the coordinates Z_W vs $\log m_W$. The loading of amine with tungsten, Z_W , is defined as moles of tungsten extracted per mole of amine at equilibrium, $Z_W = \{m_W\}_o / \{m_e^0\}_o$. The abscissa is the logarithm of the equilibrium tungsten concentration in the aqueous phase, m_W mol/kg H_2O . In Fig. 1b, the same data are depicted with a modified initial tungsten concentration, x_W^0 , as abscissa. This quantity is defined as $x_W^0 = m_W^0 G_{aq}^0 / \{G_d\}_o$. Here m_W^0 is the initial tungsten concentration in the aqueous phase, G_{aq}^0 and $\{G_d\}_o$ are the mass of water in this phase and the mass of diluent in the organic phase, respectively. According to this definition x_W^0 is m_W^0 reduced to the mass ratio of diluents equal to unity. Because of limited solubility of sodium tungstate in water the maximum initial tungsten concentrations used were $m_W^0 = 2$ mol/kg H_2O . Higher equilibrium tungsten concentrations were reached by increasing the aqueous to organic phase ratio.

In Fig. 1b the steeply ascending part of the isotherms corresponds to the region of excess of amine sulfate in the initial organic phase. In this region the distribution coefficients of tungsten are high and most of the tungsten present in the initial aqueous phase is extracted. The following balance of tungsten approximately holds

$$\{m_W\}_o \{G_d\}_o \cong m_W^0 G_{aq}^0; \quad x_W^0 \cong \{m_W^0\}_o, \quad (9)$$

i.e., x_W^0 approximates the equilibrium concentration of tungsten in the organic phase. Therefore, the isotherms in this region are almost linear with the slope $1/\{m_e^0\}_o$ (see the straight line in Fig. 1b). As can be seen in Fig. 1a, the steep parts of the isotherms for pH 3.5 and 4.5 are shifted to the right with respect to the isotherm for pH 2.5. This indicates that the equilibrium constants of the ion exchange reactions (6), (7) decrease with increasing pH.

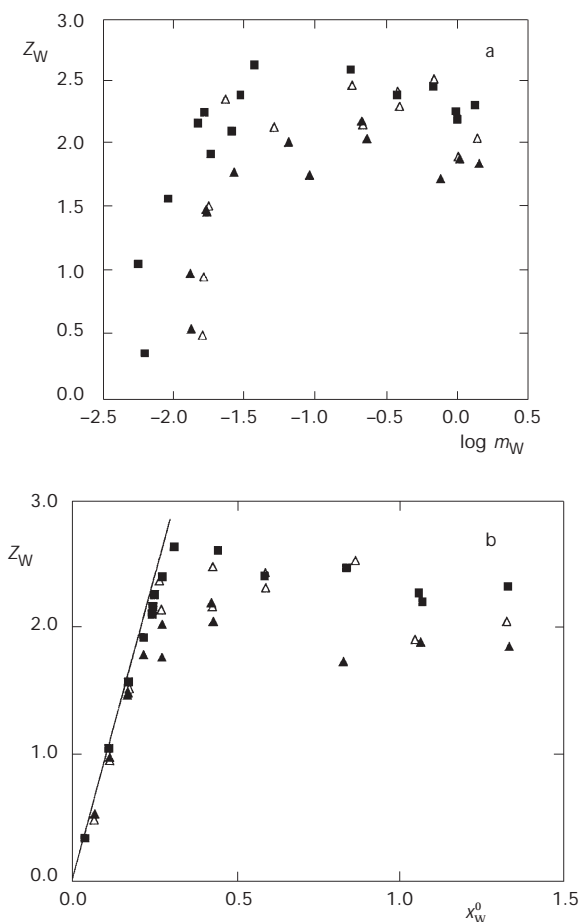


FIG. 1

Effect of pH on tungsten extraction, shown in the coordinates Z_W vs $\log m_W$ (a) and Z_W vs x_W^0 (b). $\{m_e^0\}_o = 0.1$ mol/kg diluent. pH: ■ 2.5, △ 3.5, ▲ 4.5

The isotherms in the range of tungsten concentrations $m_W > 0.06$ mol/kg H_2O are flat. The maximum values of loading for the individual isotherms decrease with increasing pH; they are approximately 2.6, 2.5 and 2.2 for pH 2.5, 3.5 and 4.5. According to the above considerations, the value of the maximum loading should be equal to the reciprocal value of the number of negative charges per tungsten atom in the average polyanion extracted. These values are 1.2 for the anion $HW_6O_{21}^{5-}$, 2.0 for $H_2W_{12}O_{40}^{6-}$ and 3.0 for

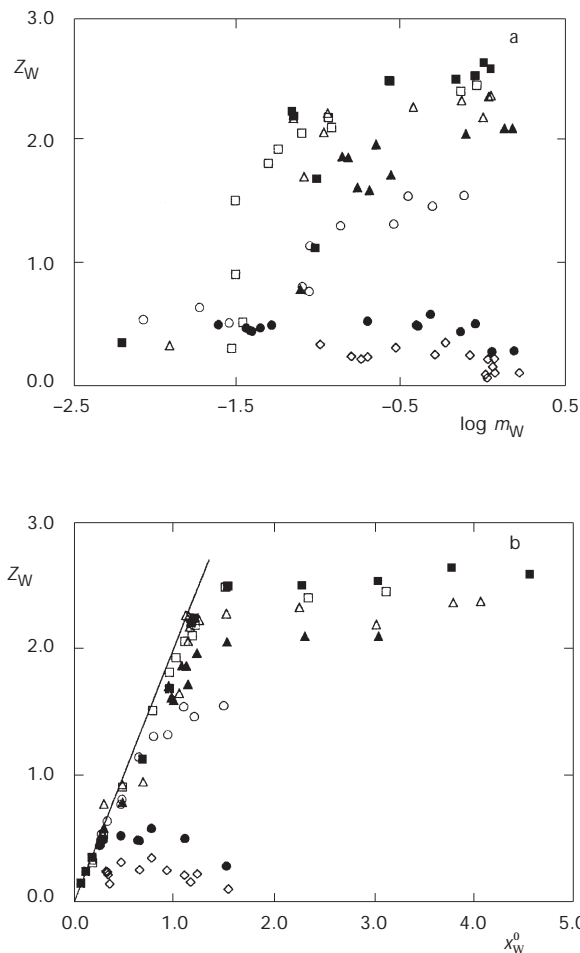


FIG. 2

Effect of pH on tungsten extraction, shown in the coordinates Z_W vs $\log m_W$ (a) and Z_W vs x_W^0 (b). $\{m_e^0\}_o = 0.5$ mol/kg diluent. pH: \square 2.0, \blacksquare 2.5, \triangle 3.5, \blacktriangle 4.5, \circ 5.0, \bullet 5.5, \diamond 6.0

$H_4W_{12}O_{40}^{4-}$. The fact that the maxima for pH 2.5–4.5 exceed 2.0 indicates that the last polyanion is also present among the extracted species.

Further extraction experiments were made with 0.5 mol/kg diluent of TAA in the organic phase and in the pH range 2.0–6.0. The results are shown in Figs 2a, 2b. In Fig. 2b, the slopes of the linear parts of the isotherms are now five times lower than in Fig. 1b, in accord with the material balance. The maximum loadings at pH 2.5, 3.5 and 4.5 have not changed significantly. At pH > 4.5, a rapid drop in the maximum loading takes place. At pH 5.0, the maximum loading $Z_W \cong 1.6$ indicates predominance of $HW_6O_{21}^{5-}$, among the extracted polyanions. At pH 6.0, Z_W is even lower than 0.5, a value corresponding to the extraction of tungstate anions WO_4^{2-} . Apparently, at this pH, the decomposition of ammonium sulfate, Eq. (6), significantly contributes to the overall effect.

Figure 3 shows the dependencies of the equilibrium sulfuric acid concentration in aqueous phase, m_{sa} , and the loading of amine with sulfuric acid, Z_{sa} , on x_W^0 for $\{m_c^0\}_o = 0.5$ mol/kg diluent and pH 2.5. The data on the sulfuric acid loading have a large scatter; nevertheless, a steeply descending part of the isotherm for sulfuric acid can be observed at low initial tungsten contents. This part corresponds to the linear section of the tungsten isotherms in Fig. 2b and reaches the value $Z_{sa} = 0$ at about the end point of this region. A section with virtually no acid in the organic phase follows. The curve for m_{sa} has a linearly ascending part in the region of an excess of

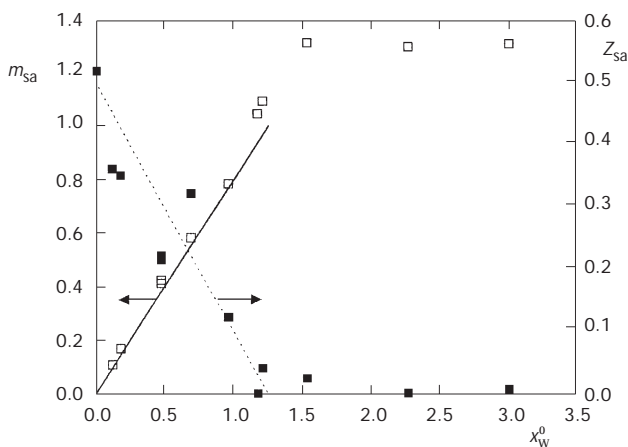


FIG. 3

Sulfuric acid content in aqueous and organic phases at equilibrium. $\{m_c^0\}_o = 0.5$ mol/kg diluent; pH 2.5. \square m_{sa} , \blacksquare Z_{sa}

TAA sulfate in initial organic phase, since the concentration of sulfate and hydrogensulfate anions in the aqueous phase should be approximately proportional to the concentration of sodium cations and protons present. The flat part of the curve corresponds to the region of a constant initial tungsten concentration, where only the ratio of the aqueous-to-organic phase varies.

In the experiments with $\text{pH} > 4.5$ and at equilibrium tungsten concentration $m_{\text{W}} > 0.2 \text{ mol/kg H}_2\text{O}$, white crystals formed in the aqueous phase about 10 h after the separation of phases. These points of isotherms $\text{pH } 5.0, 5.5$ and 6.0 were analysed before the crystals had formed and do not represent the true equilibrium. This effect is probably due to slow formation of the dimeric polyanion $\text{W}_{12}\text{O}_{41}^{10-}$.

Comparison with Literature

The position of the pH region with steeply descending tungsten extraction agrees with the results of Zelikman *et al.*¹², who extracted aqueous solutions of sodium tungstate with solutions of TAA, or trioctylamine, in kerosene with octanol at constant initial tungsten concentration. They found a steep descent of extraction at $\text{pH } 4.5\text{--}5.5$. At $\text{pH } 2.0$, they found a maximum loading of amine $Z_{\text{W}} = 3.1$ and ascribed it to the formation of polyanions $\text{H}_2\text{W}_{12}\text{O}_{39}^{4-}$. The effect of pH on the maximum values of Z_{W} is in a good

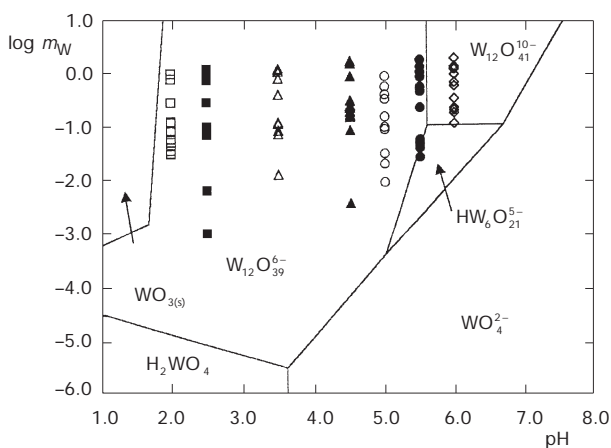


FIG. 4

Diagram of prevalent tungstate anions in aqueous phase ($t = 50 \text{ }^\circ\text{C}$; ionic strength, $I = 3 \text{ M}$)⁸. Points show experiments at $\{m_c^0\}_o = 0.5 \text{ mol/kg}$ diluent

agreement with the pH ranges of the formation of individual polyanions reported by Voldman and Zelikman⁴. The series of data from Figs 2a, 2b are also depicted in the prevalence diagram for tungsten polyanions presented by Baes and Mesmer¹⁰ (Fig. 4) to show their position in the pH-concentration area. As can be seen, particularly the data series for pH 5.0 indicates that the boundary of prevalence region of polyanions $\text{HW}_6\text{O}_{21}^{5-}$ and $\text{H}_2\text{W}_{12}\text{O}_{42}^{10-}$ may be shifted to lower pH values. The data on tungsten extraction with Primene JMT dissolved in benzene with 10% of octanol presented by Schrötterová and Nekovář¹³ were measured at constant initial pH values 2.93, 4.77, 6.28 and 8.68. The equilibrium pH values of the isotherms increased with tungsten concentration and at their end points reached approximately the respective initial values. The maximum loading was $Z_W = 2.0$ at pH 2.93, $Z_W = 1.4$ at pH 4.77 and $Z_W = 1.25$ at pH 6.28, accordingly lower than in the present work in the first two cases, but much higher in the third case. This finding is in agreement with the generally accepted notion that primary amines can effectively extract metallic anions at higher pH values than tertiary amines. In a review on commercial processes for tungsten and molybdenum, McInnes and Kim¹¹ presented results from a two-stage countercurrent laboratory extraction of aqueous sodium tungstate with a mixture of 12 vol.% Alamine 336, 12 vol.% TBP and 75 vol.% kerosene, saturated with sulfuric acid. Their distribution data at pH 2.0 show maximum loading of amine $Z_W \cong 1.8$ at the aqueous concentration 0.8 mol/l, significantly lower than those obtained in the present work.

CONCLUSIONS

The present experiments have confirmed, that tungsten can be effectively extracted from aqueous solution of pH 2.0–4.5 with trialkylamines dissolved in the mixed diluent TBP–kerosene presaturated with sulfuric acid. With 40% weight TBP, formation of the third phase can be prevented in the whole concentration range examined.

It has been confirmed that in the above pH range, the extraction mechanism is an ion exchange. With initial amine concentrations 0.1 and 0.5 mol/kg diluent loadings of TAA up to 2.5 can be reached. Further increase of aqueous phase concentration has no significant effect on the amine loading.

A rapid drop in tungsten extraction occurs at pH > 4.5, in accord with the decreasing degree of polymerization of tungsten anions formed. A significant amine sulfate decomposition has been observed at pH 6.0.

This study was supported by the Grant Agency of the Czech Republic (Grant No. 104/98/1440).

SYMBOLS

G_{aq}^0	mass of water in initial aqueous phase, kg
$\{G_{\text{d}}\}_o$	mass of diluent in organic phase, kg
m_i	concentration of the component i in aqueous phase, mol/kg H ₂ O
$\{m_i\}_o$	concentration of the component i in organic phase, mol/kg diluent
$\{m_e^0\}_o$	initial concentration of TAA in organic phase, mol/kg diluent
m_{W}^0	initial concentration of tungsten, mol/kg H ₂ O
p	degree of polymerization
q/p	degree of protonation
TAA	trialkylamine
TBP	tributyl phosphate
x/p	degree of dehydration
$x_{\text{W}}^0 = m_{\text{W}}^0 G_{\text{aq}}^0 / \{G_{\text{d}}\}_o$	modified initial molality of tungsten, mol/kg H ₂ O
$y = (2p - q)/p$	number of negative charges per tungsten atom
$Z_i = \{m_i\}_o / \{m_e^0\}_o$	loading of amine with species i

Subscripts

aq	water
e	trialkylamine
o	organic phase
sa	sulfuric acid
W	tungsten

Superscript

0	initial conditions
---	--------------------

REFERENCES

- Kopleman B., Smith J. S.: *Kirk-Othmer Encyclopedia of Chemical Technology*, 2nd ed., Vol. 22, p. 334. John Wiley & Sons, New York 1970.
- Ritcey G. M., Ashbrook A. W.: *Solvent Extraction*, Part II. Elsevier, Amsterdam 1980.
- Lassner E., Ortner H., Fichte R. M., Wolf H. U. in: *Ullmanns Encyklopädie der technischen Chemie*, 4th ed., Vol. 24, p. 457. Verlag Chemie, Weinheim 1983.
- Voldman G. M., Zelikman A. N.: *Zh. Neorg. Khim.* **1993**, 38, 1234.
- Schrötterová D., Nekovář P.: *Chem. Papers* **2000**, 6a, 393.
- Tchitchagova G. H., Ivanov I. M., Gindin L. M., Basov A. S., Tchernikov L. S.: *Izv. Sibir. Otd. Akad. Nauk SSSR* **1972**, 2, 65.
- Kim T. K., Mooney R. W., Chiola V.: *Sep. Sci.* **1968**, 3, 467.
- Yatsimirskii K. B., Romanov V. F.: *Zh. Neorg. Khim.* **1964**, 9, 1578.
- Souchay P., Boyer M., Chauveau F.: *Pure Appl. Chem.* **1972**, 34, 161.

10. Baes C. F., Jr., Mesmer R. E.: *The Hydrolysis of Cations*, p. 258. John Wiley & Sons, New York 1976.
11. Zelikman A. N., Voldman G. M., Rakova N. N., Stenyuchkina T. P.: *Cvetnye Metally* **1972**, 38.
12. MacInnis M. B., Kim T. K. in: *Handbook of Solvent Extraction* (Teh C. Lo, M. H. I. Baird and C. Hanson, Eds), p. 689. John Wiley & Sons, New York 1983.
13. Schrötterová D., Nekovář P.: *J. Radioanal. Nucl. Chem.* **2000**, 246, 671.