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Low-Molecular Weight Alcohols as Colour Stabilizers in the Spectrophotometric Determination of Extracted Molybdenum-Thiocyanate Species

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Molybdenum(VI) was reduced to its pentavalent state by ascorbic acid in the hydrochloric acid medium. The diminishing orange-red colour of the unstable molybdenum(IV)-thiocyanate complex was stabilized by addition of low alcohols and by extraction either into chloroform or into butanol. Spectrophotometric measurements followed the extraction procedure. All the investigated systems obeyed Beer's law (λ_{max} = 465 nm), molar absorptivities covering the range from 1.40×10^4 to 3.1×10^4 l mol^{-1} cm^{-1}, depending on the system type. Based on the equilibrium shift method, a reaction mechanism is proposed with $MoO(NCS)_3$ as the extracted spicies solvated by each of the alcohols added.

INTRODUCTION

Molybdenum is a metal of wide chemical and biological interest. It occurs in ores and has a large industrial application. In trace amounts, its presence is ubiquitous; it is found in water, soil and air, as well as in plants, animals and humans. Therefore, although it has been widely investigated, the interest in its chemistry does not diminish.

Molybdenum is known to exist in various oxidation states, the hexavalent being the highest one. Its solution chemistry is rather complicated.[1,2] There is a possibility of various species existing in aqueous solution,[3] and new reagents are still introduced[4] for molybdenum(VI) determination. In the molybdate solutions, molybdenum can be reduced by different reducing agents, but only ascorbic acid leads the reduction to just molybdenum(V). In the pentavalent state, molybdenum forms an orange-red thiocyanato complex with the maximum absorbance wavelength near 470 nm. Its colour is fairly unstable and diminishes even after extraction into chloroform. Among the reagents that were added to stabilize the colour, some alcohols were also investigated, but in combination with other reducing agents or various extractants.

Alcohols are a special group among the oxygen-bearing solvents. They extract inorganic species mostly by solvation, coordinating the solvent molecules to the central atom often through a water-molecule bridge.[5] Solvents are chararacterized by functional groups, their properties being most strongly exhibited by the lower homologues. The particular behaviour of the water-immiscible higher alcohols is caused by the amphoteric nature of the hydroxyl group, most similar to that of water. It governs its solvating capacity, solvent characteristics and extractability. An appreciable change in the individual phase volumes is often observed when water or aqueous electrolyte solution are equilibrated with the solvent. Mutual solubility is affected by all the constituents of the extraction system. A change in phase volumes, as a result of the change in solvent solubility in the aqueous phase solution leads to a modification of the media, both the aqueous and the organic ones. The solubilizing power of oxygenated solvents is also related to steric factors. In any particular homologous series of solvents, it is determined by the length of the hydrocarbon skeleton rather than by the strength of the metal-oxygen bond. Solubilities, as a rule, decrease with the increasing carbon-to-oxygen ratio.

The present paper deals with the experimental results of the addition of methanol, ethanol, propanol, isopropanol, butanol and isobutanol to the molybdenum(V)-thiocyanate complex. Prior reduction of molybdenum(VI) was performed in the hydrochloric acid medium by ascorbic acid, which is known to reduce molybdenum only to its pentavalent state. Alcohols stabilize the colour of the thiocyanate complex and make it applicable for extraction and for spectrophotometric measurements.

EXPERIMENTAL

All chemicals were of the *p.a.* purity grade.

The molybdenum(VI) solution (c = 1.00 × 10^{-2} mol dm^{-3}) was an ammonium molybdate aqueous solution standardized gravimetrically by 8-hydroxyquinoline.[6] The molybdenum working solutions were prepared by dilution.

The ascorbic acid solution was prepared in deionized water. Relatively small amounts of the solution were freshly prepared to avoid the effect of decomposition of the ascorbic acid solution by standing.

As a source of thiocyanate ions, an aqueous solution of either sodium or potassium thiocyanate was used. This caused no difference regarding the absorbance measurements of the extracted systems.

The systems were generally prepared by the addition of components in the following order: molybdenum(VI), hydrochloric acid, ascorbic acid, thiocyanate ion, alcohol, chloroform. Before addition of the extracting solvent, the prepared aqueous phases were allowed to stand for approximately 10 minutes so as to accomplish a complete reduction of molybdenum(VI). Although extraction into the organic phase was achieved after shaking the solutions for about one minute (colour transferred from the aqueous to the organic layer), the systems were equilibrated for 5–10 minutes.

Three types of extraction systems were investigated. In the first type, methanol (5 ml), ethanol (5 ml), propanol (1.5 ml) or isopropanol (1.5 ml) were added into the aqueous phase, making up the total aqueous phase volume of 10 ml. Extraction was performed with 5 ml of $CHCl_3$. Volume measurements after extraction revealed an approximately equal distribution of alcohol between the phases. The second type of extraction systems involved addition of butanol (2.5 ml) or isobutanol (2.5 ml) into the chloroform layer (2.5 ml), making up the total organic phase volume of 5.0 ml. The total volume of the aqueous phase was 5.0 ml, as well. There was no change regarding the initial volumes observed after the extraction. In the third extraction system, the aqueous solution (5.0 ml) was extracted with 5.0 ml of pure butanol, or of isobutanol.

Optimal concentration ranges of all components involved in the extraction systems were examined with molybdenum concentrations in the aqueous phase of 2.5×10^{-5} M or 5×10^{-5} M. The influence of other system components upon the absorbance values was examined in the concentration ranges: 0.01 – 6 M HCl, 0.01 – 0.9 M thiocyanate ion, 0.01 – 1% ascorbic acid. The validity of Beer's law was investigated in the molybdenum concentration range of $1 \times 10^{-6} - 1 \times 10^{-4}$ M.

A Perkin-Elmer Model 200 spectrophotometer was used for spectrophotometric measurements.

RESULTS AND DISCUSSION

The extraction procedure preceded the spectrophotometric determination of molybdenum(V)-thiocyanate species. Since the solubility and miscibility of the added alcohols both in water and in chloroform singnificantly differ, three types of extraction systems were studied.

The first type of extraction system was the one in which water- and chloroform-miscible alcohols (methanol, ethanol, propanol, isopropanol) were added to the molybdenum(V)-thiocyanate complex formed in the aqueous phase. The complex was afterwards extracted into chloroform. Extraction dependences of the coloured complex on the concentrations of all components involved were determined spectrophotometrically. Each investigated component was varied while all the others were either in excess or at their optimal values with regard to the constant molybdenum concentration. The mutual water-alcohol and chloroform-alcohol miscibility followed by unmeasurable volume changes, especially by methanol and ethanol, unabled the system analytical concentrations to be expressed other than as initial concentrations.

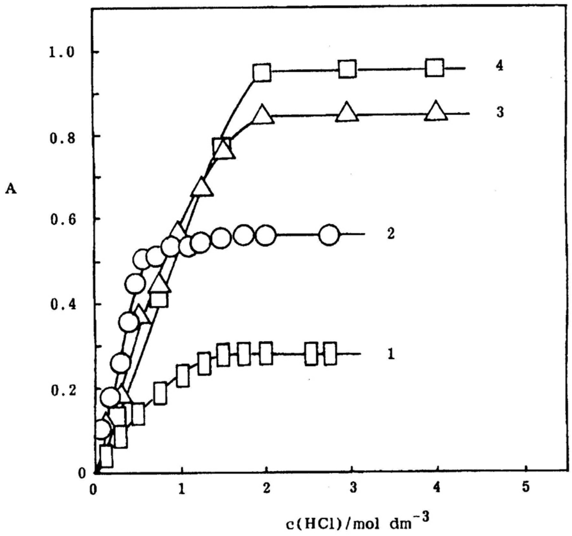

Figure 1. Influence of hydrochloric acid concentration on the absorbance of the extracted systems. Concentrations: 2.5×10^{-5} M Mo(VI), 0.37 M NaNCS, 0.3% ascorbic acid. Alcohols added: (1) methanol (50%), (2) ethanol (50%), (3) propanol (15%), (4) isopropanol (15%). λ_{max} = 465 nm.

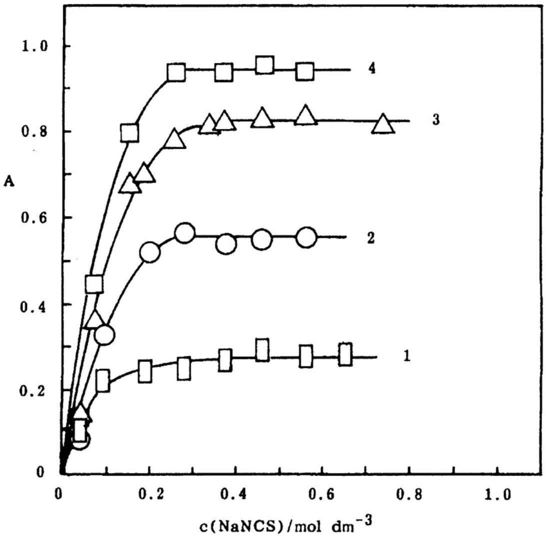

Figure 2. Dependence of the absorbance of the extracted complex on the thiocyanate ion concentration. Concentrations: 2.5×10^{-5} M Mo(VI), 2 M HCl, 0.3% ascorbic acid. Alcohols added: (1) methanol (50%), (2) ethanol (50%), (3) propanol (15%), (4) isopropanol (15%). λ_{max}= 465 nm.

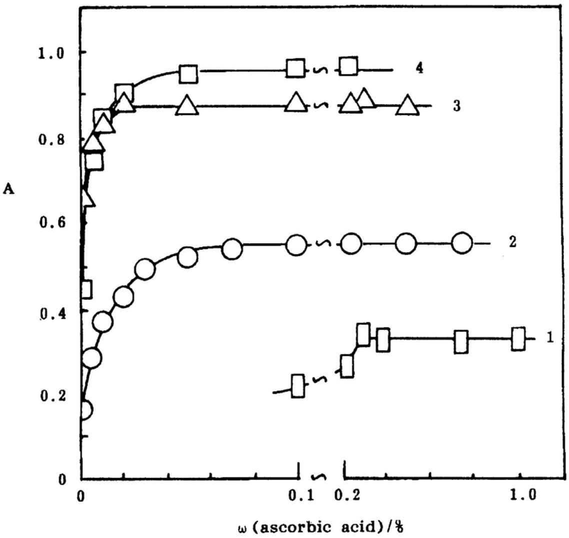

Figure 3. Excess of ascorbic acid needed for complete reduction of molybdenum(VI). Concentrations: 2.5×10^{-5} M Mo(VI), 2 M HCl, 0.46 M NaNCS. Alcohols added: (1) methanol (50%), (2) ethanol (50%), (3) propanol (15%), (4) isopropanol (15%). λ_{max} = 465 nm.

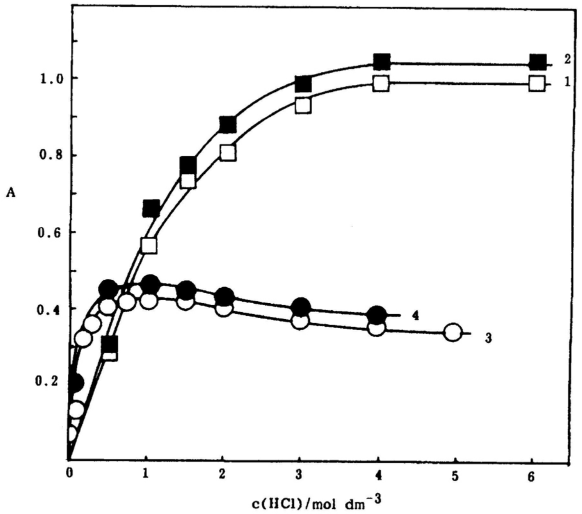

Figure 4. Acidity dependence for the extraction of the molybdenum(V)-thiocyanate complex in the systems containing butanols. Concentrations: 5×10^{-5} M Mo(VI), 0.46 M thiocyanates, 0.2% ascorbic acid, 50% alcohols. Alcohols added: (1) butanol, (2) isobutanol. Concentrations: 2.5×10^{-5} M Mo(VI), 0.31 M thiocyanates, 0.2% ascorbic acid. Extraction into pure alcohols: (3) butanol, (4) isobutanol. λ_{max} = 465 nm.

The extraction dependence on the hydrochloric acid concentration with all other system components in excess with regard to molybdenum (Figure 1) revealed that different acidities were needed to achieve maximum absorbance values. At acid concentrations greater than 2 M, absorbances of the organic phase always reached constant values. Changes in the thiocyanate concentrations (Figure 2) caused differences in the constant absorbance values region for each of the alcohols added. At a concentration higher than 0.3 M thiocyanate, there was no change in the extraction efficiency. Ascorbic acid (Figure 3) secured complete molybdenum reduction at very low concentrations (< 0.1% *w*/*v*), except in the system with methanol, where the constant absorbance region started at 0.3% *w*/*v* ascorbic acid. With addition of methanol, the lowest homologue of added alcohols, only a partial extraction of the formed complex into chloroform was achieved. Although maximum extraction was indicated by constant absorbance values of the organic phase, attained by addition of each single system component (Figures 1, 2, 3), the aqueous phase as well as the chloroform solution were orange-red after equilibration. The measured absorbances were of about the same value, indicating approximately equal distribution of the coloured complex between the two phases. The influence of the initial alcohol volume changes in the aqueous phase showed appreciable differences, depending on the nature of the alcohol used. Addition of methanol caused a continuous increase in absorbance over the entire investigated volume region, but complete extraction was not attained. Ethanol and propanols led the extraction to completeness, showing regions of maximum absorbances with colourless aqueous phases (50% ethanol or 15% propanols regarding the aqueous phase volumes).

In the second type of extraction system, stabilization of the molybdenum(V)-thiocyanate complex colour was achieved by addition of butanol or isobutanol to the chloroform. Volume measurements of both phases after equilibration showed no differences from the initial volumes. This points to the major solubility of the complexes solvated by butanols in chloroform. Addition of 50% *v*/*v* of each butanol to the chloroform phase provided the best extraction conditions for the molybdenum(V)-thiocyanate complex. All system components influenced the extraction of the complex into the organic phase. The plateau in absorbance values described the optimal concentration range of each single component. The optimal hydrochloric acid concentration was above 4 M (Figure 4). An excess of thiocyanate corresponding to approximately 0.4 M was needed to achieve a complete colour development (Figure 5). More than 0.1% ascorbic acid had to be used for complete reduction of molybdenum(VI) (Figure 6).

Immiscibility of butanol and isobutanol with water, as well as the extractability of the molybdenum(V)-thiocyanate complex into the butanol-chloroform mixture gave rise to investigations of the molybdenum(V)-thiocyanate complex extraction into pure butanols. In this third type of extraction system,

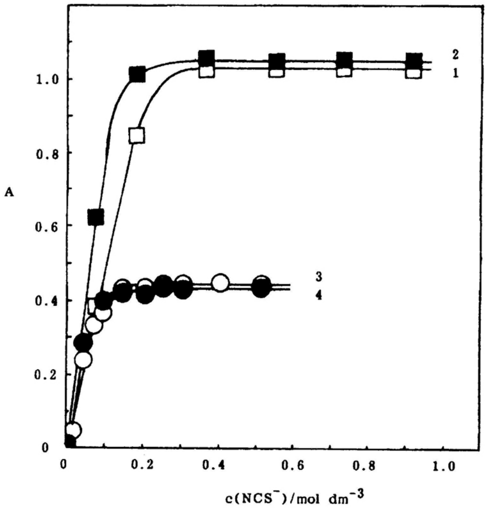

Figure 5. Influence of thiocyanate ions on the extraction of the molybdenum(V)-thiocyanate complex in the presence of butanols. Concentrations: 5×10^{-5} M Mo(VI), 6 M HCl, 0.2% ascorbic acid, 50% alcohols. Alcohols added: (1) butanol, (2) isobutanol. Concentrations: 2.5×10^{-5} M Mo(VI), 1.5 M HCl, 0.2% ascorbic acid. Extraction into pure alcohols: (3) butanol, (4) isobutanol. λ_{max} = 465 nm.

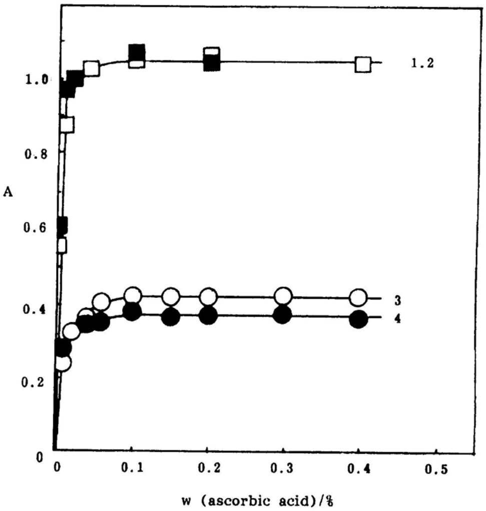

Figure 6. Concentration of ascorbic acid needed for a complete reduction of molybdenum(VI). Concentrations: 5×10^{-5} M Mo(VI), 6 M HCl, 0.46 M thiocyanates, 50% alcohols. Alcohols added: (1) butanol, (2) isobutanol. Concentrations: 2.5×10^{-5} M Mo(VI), 1.5 M HCl, 0.31 M thiocyanates. Extraction into pure alcohols: (3) butanol, (4) isobutanol. λ_{max} = 465 nm.

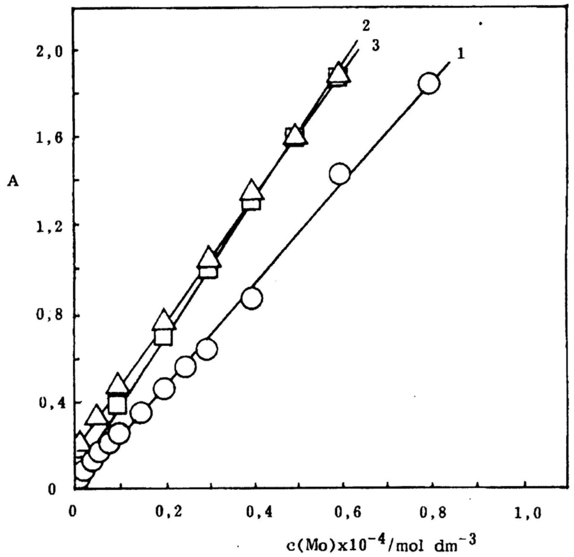

Figure 7. Validity of Beer's law in the extracted systems with ethanol and propanols added. Concentrations: 2 M HCl, 0.37 M NaNCS, 0.2% ascorbic acid. Alcohols added: (1) ethanol (50%), (2) propanol (50%), (3) isopropanol (15%). λ_{max} = 465 nm.

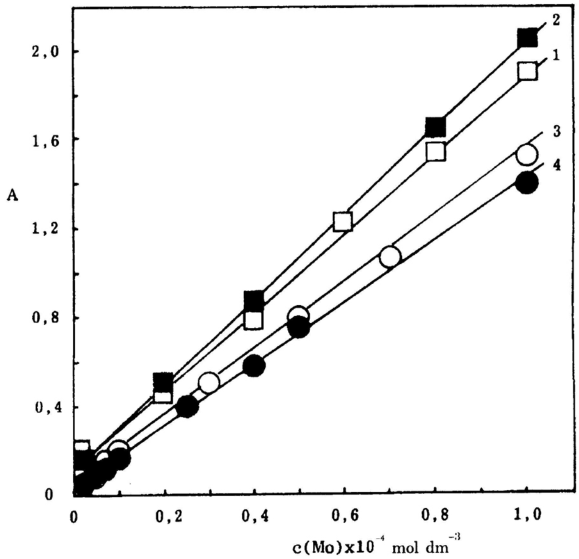

Figure 8. Validity of Beer's law in the extracted systems involving butanols. Concentrations: 6 M HCl, 0.93 M thiocyanates, 0.2% ascorbic acid, 50% alcohols. Alcohols added: (1) butanol, (2) isobutanol. Concentrations: 1.5 M HCl, 0.31 M thiocyanates, 0.2% ascorbic acid. Extraction into pure alcohols: (3) butanol, (4) isobutanol. λ_{max} = 465 nm.

the orange-red complex formed in the aqueous phase was quantitatively transferred into the butanol phase during equilibration. The acidity dependence (Figure 4) revealed a plateau of maximum absorbance at about 1 M HCl, whereafter the measured values showed a slight decrease. Maximum extraction was achieved at concentrations higher than 0.3 M thiocyanate (Figure 5) and 0.1% ascorbic acid (Figure 6). There were many thiocyanato-forming metal ions whose presence in the aqueous solution could have caused interferences with the spectrophotometric determination of molybdenum because of possible coextraction. Among them, cobalt(II) and iron(III) were chosen, and their influence upon the spectrophotometric determination of molybdenum(V)-thiocyanate after extraction into butanols was examined. In the investigated concentration range (1.1×10^{-7} – 1.1×10^{-3} M Fe^{3+}; 8.8×10^{-8} – 8.8×10^{-4} M Co^{2+}), the two foreign ions did not influence either the shape and position of the absorption spectrum or the absorbance values of the molybdenum complex measured under optimal component concentrations. This indicates the possibility of determining molybdenum(V) by measuring the absorbance of its thiocyanate complex in the presence of cobalt(II) and iron(III).

All the investigated system types were spectrophotometrically stable within 24 hours, except for the one to which methanol was added. Not only was it characterized by colour instability but it also failed to achieve complete extraction.

The maximum wavelength of investigated colour was the same (465 nm) for all types of the extraction systems, indicating the existence of the same complex species regardless of the alcohol added. However, addition of alcohols obviously influenced the colour intensity and thereby the sensitivity of the method.

TABLE I

Molar absorptivities, Sandel's sensitivity, number of bound thiocyanate groups and conditional formation constants

System*	ε mol^{-1}lcm^{-1}	Sandel's sensitivity µg cm^{-2}	n	log K_f
Mo-HCl-NCS-AA-EtOH-$CHCl_3$	1.94×10^4	0.0049	2.63	3.02
Mo-HCl-NCS-AA-(*n*-PrOH)-$CHCl_3$	2.80×10^4	0.0034	2.70	2.90
Mo-HCl-NCS-AA-(*i*-PrOH)-$CHCl_3$	3.10×10^4	0.0031	2.70	2.90
Mo-HCl-NCS-AA-(*n*-BuOH)-$CHCl_3$	1.80×10^4	0.0053	2.70	2.90
Mo-HCl-NCS-AA-(*i*-BuOH)-$CHCl_3$	2.06×10^4	0.0046	2.94	3.66
Mo-HCl-NCS-AA-(*n*-BuOH)	1.45×10^4	0.0066	2.94	3.66
Mo-HCl-NCS-AA-(*i*-BuOH)	1.40×10^4	0.0068	2.86	3.97

* Symbols: Mo = Mo(VI); AA = ascorbic acid; NCS = thiocyanate ion; EtOH = ethanol; *n*-PrOH = propanol; *i*-PrOH = isopropanol; *n*-BuOH = butanol; *i*-BuOH = isobutanol

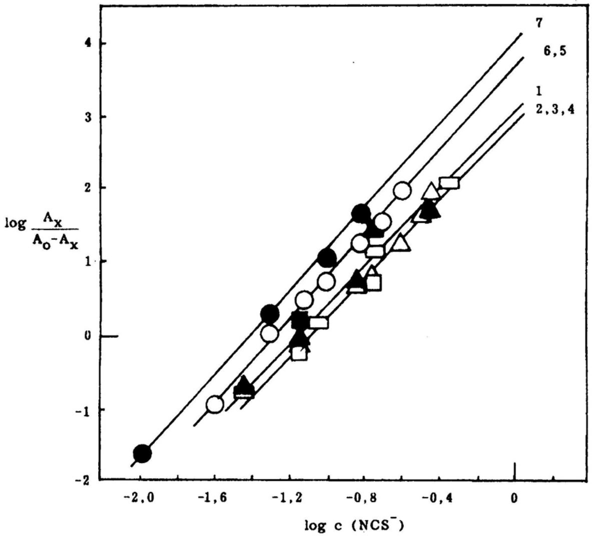

Figure 9. The equilibrium shift method for determination of the composition of the molybdenum(V)-thiocyanate species. Concentrations according to Figures 2 and 5. Alcohols added: (1) ethanol, (2) propanol, (3) isopropanol, (4) butanol, (5) isobutanol. Extraction into pure alcohols:(6) butanol, (7) isobutanol. λ_{max} = 465 nm.

Beer's law was obeyed (Figure 7, Figure 8) in the whole range of the investigated molybdenum concentrations ($1 \times 10^{-6} - 1 \times 10^{-4}$ M). Care must be taken to let the solutions with higher molybdenum concentrations ($> 7 \times 10^{-5}$ M), in the presence of ascorbic acid, stand longer than usual (approximately 20 minutes or more) so as to achieve complete reduction of the metal before extraction. The molar absorptivity and Sandel's sensitivity values are summarized in Table I, their average magnitude being in agreement with the generally accepted absorptivity and sensitivity values.

As very high thiocyanate concentrations were needed for colour development, the only way to elucidate the composition of the extractable complex was the equilibrium shift method[7] (Figure 9). The slopes of the straight lines indicate the number of bonded thiocyanate ions and the intersection with the ordinate corresponds to the value of the conditional formation constant. Symbol A_0 indicates maximum absorbance of the measured system, and A_x is the measured value before the complete complex formation is reached. According to the experimental results, listed in Table I, there are three thiocyanate groups attached to the molybdenum(V) central metal ion (n_{avg} = 2.79) regardless of which alcohol was added. Conditional formation constants change with the experimental conditions within approximate limits $\log K_f = 3.29 \pm 0.43$. On the basis of the experimental results, one could presume a general reaction mechanism between molybdenum(V) and thiocyanate ions, regardless of the alcohol used as colour stabilizer:

$$MoO^{3+}{}_{aq} + 3\ NCS^{-}{}_{aq} \leftrightarrow MoO(NCS)_{3\ org}$$

Most likely alcohols just solvatize the complex and enhance its solubility in the organic phase, at the same time preventing the back-oxidation of molybdenum(V) and decomposition of the coloured complex.

The thiocyanate method for the spectrophotometric determination of molybdenum is the oldest and still the most widely used one, despite a number of limiting factors. Molybdenum(V) forms an orange-red complex with the thiocyanate ion in acid solution with an absorbance maximum near 470 nm, depending upon other system conditions. Molybdenum(VI) needs to be reduced to the pentavalent state to produce the coloured complex. Several molybdenum(V)-thiocyanate complexes exist, with different assigned formulas, for instance oxopentathiocyanatomolybdate(V) ion, $/MoO(NCS)_5/^{2-}$, and a dimeric species, perhaps $/(MoO)_2(NCS)_6/^{4-}$.[1] Molybdenum can react with the thiocyanate ion in the chloride acid medium giving complexes with a different number of bonded thiocyanate ions, the general formula being $/Mo(NCS)_n/^{5-n}$.[2] On the other hand, the main species existing in the hydrochloric acid medium might be MoO^{3+}, reacting with thiocyanates and giving complexes of the type $MoO(NCS)_{n3-n}$.[1] The molybdenum(V)-thiocyanate complex can be extracted into an organic solvent before determination. In order to stabilize the complex colour, some other reagents can be added to the system, forming stable ternary complexes,[1,2] for instance α-benzoinoxime,[8] tetraphenylonium salts,[9] monooctyl-α-anilinobenzylphosphonic acid,[10] perazine dimalonate,[11] chlorpromazine hydrochloride.[7] Different molybdenum(V)-thiocyanate species have been found to exist in the described ternary complexes. Stabilization of the developed colour was acchieved also by addition of ethanol,[12] with the existence of $H[MoO(NCS)_4] \times C_2H_5OH$. The actual molybdenum species is hard to determine, because it depends on all the system components, concentrations and characteristics.

The presented spectrophotometric method describes the determination of molybdenum in the concentration range $1 \times 10^{-6} - 1 \times 10^{-5}$ M, involving a previous reduction of molybdenum(VI) to molybdenum(V) by addition of ascorbic acid ($c > 0.1\%$), complexation with thiocyanate ions in large excess, and addition of low-molecular weight alcohols. They either participate in the chloroform extraction of the molybdenum(V)-thiocyanate species (ethanol, propanols, butanols), or can be used as extractants (butanols). In any case, they stabilize the developed colour of the thiocyanate complex, presumably $MoO(NCS)_3$, enabling spectrophotometric determination at a maximum wavelength of 465 nm. To conclude, the extraction spectrophotometric procedures described can be recommended, especially those using propanols and butanols as colour stabilizers, as simple and fast methods for the determination of molybdenum which is present in the aqueous solution in the hexavalent state.

REFERENCES

1. I. M. Kolthoff, P. J. Elving, (Eds.), *Treatise on Analytical Chemistry,* Part II, Vol 10, Interscience, New York, 1978.
2. E. B. Sandell, *Colorimetric Determination of Traces of Metals,* Third Ed., Interscience, New York, 1959.
3. M. A. Olazabal, M. M. Orive, L. A. Fernandez, J. M. Madariaga, *Solvent Extr. Ion Exch.* **10** (1992) 623.
4. Rameshwar, J. R. Mehta, *Fresenius J. Anal. Chem.* **349** (1994) 520.
5. Y. Marcus, A. S. Kertes, I*on Exchange and Solvent Extraction of Metal Complexes,* Wiley-Interscience, London, 1969.
6. A. I. Vogel, *A Text-Book of Quantitative Inorganic Analyses,* Third Ed., Longmans and Greene, London, 1961.
7. H. Puzanowska-Tarasiewicz, A. Grudniewska, M. Tarasiewicz, *Anal. Chim. Acta* **94** (1977) 435.
8. C. L. Luke, *Anal. Chim. Acta* **34** (1966) 302.
9. B. Tamhina, M. J. Herak, *Microchim. Acta I* (1976) 553.
10. B. Tamhina, M. J. Herak, V. Jagodić, *Anal. Chim. Acta* **76** (1975) 417.
11. B. Keshavan, P. Nagaraja, *Microchim. Acta II* (1985) 379.
12. U. Madan, L. R. Kakkar, *Indian J. Chem.* **21A** (1982) 326.

SAŽETAK

Niži alkoholi kao stabilizatori boje pri spektrofotometrijskom određivanju ekstrahiranja molibdenova tiocianata

Vlasta Allegretti Živčić i Marko Herak

Molibden(VI) reduciran je askorbinskom kiselinom u klorovodično kiseloj sredini u svoje peterovalentno stanje. U nazočnosti tiocijanatnog iona nastaje tada narančastocrvena nestabilna kompleksna vrsta molibdena (V). Dodatkom nižih alkohola i ekstrakcijom, postignuta je postojanost boje, čime je omogućeno jednostavno spektrofotometrijsko određivanje molibdena. Svi istraživani sustavi u skladu su s Beerovim zakonom (λ_{max} = 465 nm), pri čemu molarni apsorpcijski koeficijenti imaju vrijednost u rasponu $1,40 \times 10^4 ... 3,10 \times 10^4$ l mol^{-1}cm^{-1}, ovisno o dodanom alkoholu. Temeljem rezultata dobivenih primjenom metode ravnotežnih pomaka predložen je reakcijski mehanizam u kojem je [MoO(NCS)$_3$] kompleksna vrsta koja se ekstrahira i stabilizira solvatacijom svakim od dodanih alkohola.