텅스텐의 아민용매 추출 과정에서의 알코올의 작용

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Alcohol-Amine Synergism in the Organic Solvent Extraction of Tungsten

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요   약 : 5 % 트리옥틸아민과 5 % 옥틸알콜이 든 핵산유기용매 1 l 는 62 g 의 WO₃를 추출할 수 있었는데 반하여 아민만을 사용했을 경우는 37 g 의 WO₃밖에 추출할 수 없었다. 유기용매 추출과정에서 이러한 알콜의 아민-텅스텐 화합물의 용해도의 상승작용 및 아민과 텅스텐산간의 상호작용을 핵자기 공명분광학을 이용하여 연구하였다. 텅스텐은 고분자형의 텅스텐산 이온상태로 유기층으로 추출되어 다중텅스텐산 트리옥틸 암모니움염을 형성함을 알 수 있었으며 이 염은 텅스텐산 이온과 알콜간에 수소결합을 형성함으로써 탄화수소 용매에서 더욱 안정화됨을 알 수 있었다.

Abstract   The organic solvent mixture of 5 % trioctylamine and 5 % n-octyl alcohol in n-hexane could be loaded with tungsten to 62 g WO_3/l whereas the amine alone could be loaded only to 37 g WO_3/l. Molecular interaction between amine and tungstate ion during the solvent extraction process and the synergistic effect of alcohol in enhancing the solubility of the amine-tungstate complex have been studied by NMR spectroscopy. Tungsten has been shown to be extracted as a polymeric tungstate ion into the organic phase to form a trioctyl ammonium polytungstate salt, which was more stabilized in the hydrocarbon medium by interacting with alcohol via hydrogen bonding between the tungstate ion and alcohol.

Introduction

It is well known that many anions[1-6] in aqueous solution can be extracted by organic reagents such as amines, tributylphosphate, ketones, etc. Since tungsten forms large polymeric anions in the low pH range, it was demonstrated by many workers[7-11] that tungsten could be recovered from the low-grade scheelite using such organic solvents. Particularly, the solvent extraction method using bulky aliphatic amines

has already been industrialized.

In the amine-solvent extraction process a small portion of a long chain aliphatic alcohol (5-15%) is usually added as so called phase-conditioner. The alcohol is generally known to increase the loading capacity of the organic solvent. However, the mechanistic feature of such synergistic effect of alcohol in enhancing the loading capacity has not been understood. Furthermore, the chemical nature of amine-tungsten interaction has not been fully understood. In

this paper we present the results of the NMR study on the interaction between amine and tungsten and on the role of alcohol as phase-conditioner in the amine-solvent extraction process. We selected as a model organic solvent the mixture of trioctylamine (extractant) and *n*-octyl alcohol (phase-conditioner) in n-hexane.

Experimental

Materials. A simulated tungsten-pregnant solution was prepared by acidifying the $0.1 M$ aqueous sodium tungstate (Na_2WO_4) solution to pH=2.0. This solution contains 23.2 g WO_3 per liter. The practical grade trioctylamine (TOA, Eastman Kodak Co.) was used as organic extractant without further purification. The organic solvent was composed of $0 \sim 15$ % *n*-octyl alcohol (Wako Pure Chem. Ind. Ltd.) as phase-conditioner, the remainder being chemically pure *n*-hexane. *n*-Hexane was employed instead of kerosene as diluent. The other reagents were all chemical pure or better unless specified.

Solvent extraction. The organic solvent (100 ml) was loaded with tungsten by contacting it with the same volume of the aqueous pregnant solution in a separatory funnel. The two phases were separated after shaking for five minutes using a mechanical shaker and then the aqueous layer was drained off. The partly loaded organic phase may be further loaded by shaking it repeatedly with other new portions of the pregnant solution. The loading capacity of the organic solvent was determined by repeating this process until the gelatinous product started to form. If no gelatine had formed, the maximum amount of tungsten which could be loaded in the specified organic solvent was regarded as its loading capacity. The total amount of tungsten extracted was estimated by analyzing the aqueous layer.

Physical measurements. All the NMR spectra

were recorded on the Varian Model HA-100D NMR Spectrometer. In principle, NMR samples for preliminary study were all prepared in *n*-hexane unless specified. If the organic solvent was contacted with the aqueous phase, the samples for NMR measurement were taken after drying with anhydrous sodium sulfate.

Results and Discussion

The tungsten-loading capacity of the trioctylamine solvent depends on the concentration of *n*-octyl alcohol as shown in *Fig.* 1. The 5 % trioctylamine (ca. 0.15 M) in *n*-hexane could be loaded with tungstate to 37 g $WO_3/1$ when the phase conditioner is absent. Further attempts beyond this point resulted in a gelatinous material out of the organic layer. The loading capacity increases with the increasing content of *n*-octyl alcohol but reaches the plateau of 62 g $WO_3/1$ at 5 % alcohol concentration. Further increasing the alcohol concentration did not affect the loading capacity of the solvent. It has been observed that extractions with the 5 % amine solvent containing less than 5 % alcohol resulted in precipitation of the gelatinous product when saturated with tungstate, but the solvent with more than 5 % alcohol did not produce the gelatine even when contacted repeatedly with new portions of the pregnant solution beyond its capacity. These experimenal results imply that alcohol does not participate directly in the complex formation with tungstate, but only contribute to increasing the loading capacity, that is, the solubility of amine-tungstate complex in the organic solvent. The isolated gelatine is soluble in many organic solvents, although it can not be stripped with aqueous ammonia solution. The gelatinous product could be redissolved in the alcohol-hexane solvent and was shown to be spectroscopically same as the amine-tungstate
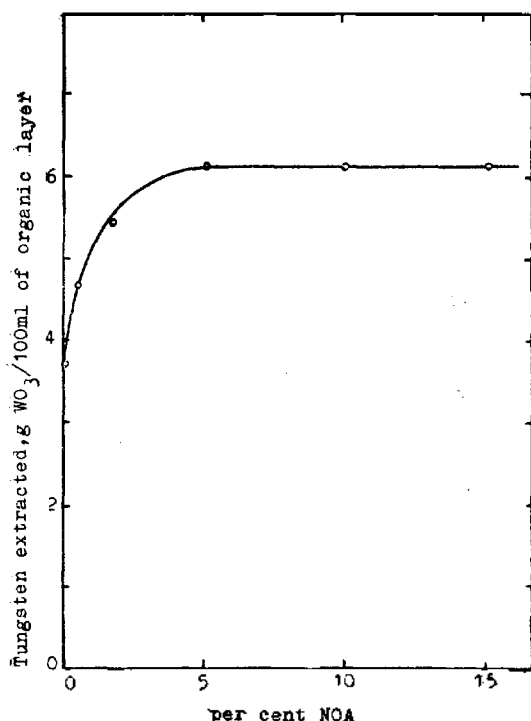
Fig. 1. Tungsten-loading capacity of 5 % TOA solvent depending on the concentration of NOA

complex in the organic phase. Further chara-cterization of this material is underway. Now it seems that the synergistic effect of alcohol to increase the loading capacity may be explicable in terms of the interaction between the amine-tungsten complex and alcohol molecules.

It should be noted in the *Fig.* 2 that alcohol has shown another aspect of its synergistic effect in addition to its increasing ability of loading capacity. In the first extraction in which 100 ml of 5 % TOA solvent (ca. 0.15 *M*) was shaken with the same volume of the tungstate solution (0.1 *M* WO$_3$) tungsten was completely extracted in all cases. However, from the second extraction the difference in the extracting efficiency is remarkable depending on the alcohol concentration. The 5 % TOA solvent containing more than 5 % alcohol has shown also complete extraction of tungsten

in the second portion of the tungstate solution whereas the amine alone could extract only less than 60 % tungsten in the second portion. Such difference in efficiency seems to be directly related to the solubility of amine-tungsten complex. Extraction efficiency is represented as the distribution coefficient of tungsten between the two layers, $K_d=\dfrac{(WO_3)\,org.}{(WO_3)\,aq.}$. Therefore, the enhanced solubility of amine-tungstate in the presence of alcohol in the organic phase would increase the coefficient and as such the extraction efficiency.

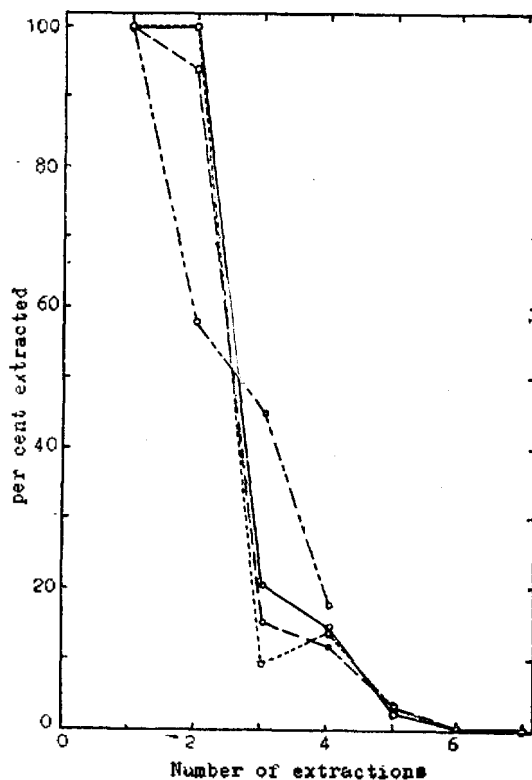In order to explain such synergistic effect of alcohol in the amine solvent extraction, NMR
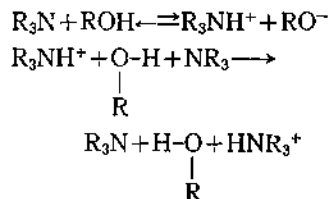

Fig. 2. Extracted fraction of tungsten at each loading step
---- TOA 5 %, *n*-Hexane 95 %
--- TOA 5 %, NOA 5 %, *n*-Hexane 90 %
— TOA 5 %, NOA 10 %, *n*-Hexane 85 %
······ TOA 5 %, NOA 15 %, *n*-Hexane 80 %

data of our model system will be discussed in detail. To understand the interaction of the tungstate with the organic solvent, we need to consider the NMR spectra of the amine and alcohol separately before any attempt to interpret the spectra of the tungsten-loaded organic solvent. It is seen in the highly resolved NMR spectra shown in *Fig.* 3 that the alcoholic proton (-OH) interacts with the amine molecule. The alcoholic proton shows a triplet in the absence of TOA but decouples into a sharp singlet when more than 1 % TOA is added while the quartet of the α-protons changes into a triplet. This means that the alcohlic proton does not stay at the alcoholic oxygen site long enough to couple with its α-protons in the presence of amine. The best speculation seems to

Fig. 3. Changes in the NMR spectra of NOA by addition of TOA. (for 10 % NOA solution in *n*-hexane)

be that there are both protonation and fast exchange[12] as we suggested in the following:

$$R_3N+ROH\longleftarrow\rightleftharpoons R_3NH^++RO^-$$
$$R_3NH^++O-H+NR_3\longrightarrow$$
$$\overset{|}{R}$$
$$R_3N+H-O+HNR_3^+$$
$$\overset{|}{R}$$

The exchange rate, r of the alcoholic proton may be calculated from the equation[12], $r=\dfrac{1}{\tau}$ $=\delta$ where τ is the mean life time between exchange events and δ is the separation of the multiplet components in cycles per second. The observed value of τ was 0.2 sec. in the solution containing 5 % NOA and 0.1 % TOA in *n*-hexane. Another important aspect to note is that the chemical shift of the alcoholic proton is strongly dependent on its concentration due to the degree of its hydrogen bonding[12] whereas that of its α-protons is almost constant (*Fig.* 4). However, the variation of TOA concentration does not affect the chemical shifts both of the alcoholic and its α-protons. It is also shown in *Fig.* 4 that the chemical shift of the amine α-protons is not variable either by the alcoholic or amine concentration.

Now we are in shape to discuss the loaded organic solvent. The changing NMR spectra of the extractant of 5%TOA and 5 % NOA in *n*-hexane during the extraction process are presented in the *Fig.* 5. When the pure organic phase of 5 % TOA and 5 % NOA (*a*, *Fig.* 5) is acidified, the alcoholic proton undergoes a dramatic down-field shift with band broadening and the amine α-protons also suffer a remarkable downfield shift with structural change as shown in *b*. *Fig.* 5. Such spectral changes strongly indicate that there is a fast proton exchange between the portonated amine and alcohol. In fact in the acidified amine solvent a new broad peak corresponding to the ammonium proton (R_3,
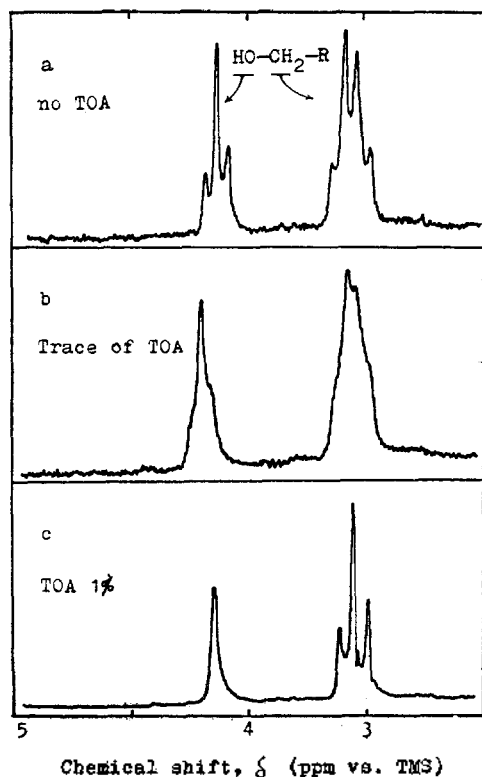
Fig. 4. Dependence of chemical shifts on the concentration of NOA or TOA

$$\left.\begin{array}{l}\text{TOA } 5\% \\ \text{NOA varying}\end{array}\right)\text{—OH}\bullet, \text{—OCH}_2\text{—O, N}\stackrel{\displaystyle /\text{CH}_2\text{—}}{\stackrel{\displaystyle -\text{CH}_2\text{—}}{\diagdown\text{CH}_2\text{—}}}\text{—}\square$$

$$\left.\begin{array}{l}\text{TOA varying} \\ \text{NOA } 5\%\end{array}\right)\text{—OH}\times, \text{—OCH}_2\text{—}\blacktriangle, \text{N}\stackrel{\displaystyle /\text{CH}_2\text{—}}{\stackrel{\displaystyle -\text{CH}_2\text{—}}{\diagdown\text{CH}_2\text{—}}}\text{—}\triangle$$
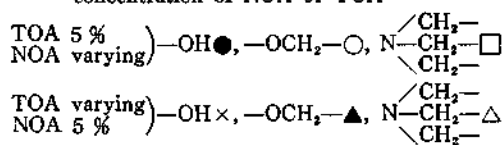
NH^+) was observed at 8.8 ppm (not shown in the figure). The chemical shift of the alcoholic proton in this case would be $N(OH) \cdot \delta(OH) + N(NH) \cdot \delta(NH)$ where N is mole fraction. When this acidified solvent was shaken with the same volume of the simulated pregnant solution (23.2 g WO_3 per liter), the alcoholic proton peak moved to higher field while the amine α-protons suffered further down-field shift with complete decoupling. This tendency continued until the solvent was loaded to its capacity which was reached when extraction was repeated six times (see also Fig. 1). The amine α-proton resonance finally appeared at 3.5 ppm where its smeared band partially overlapped with the triplet of
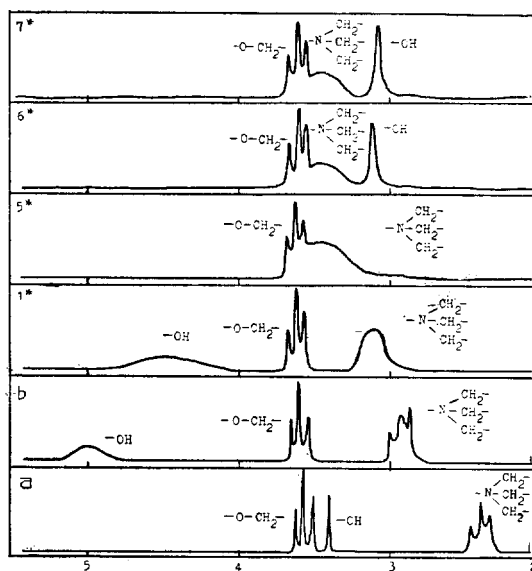

Fig. 5. The changing NMR sqectra of the solvent during the extraction process
a. Solvent (TOA 5 %, NOA 5 % in n-hexane)
b. Acidified solvent
*The numbers indicate the number of times extractions with new portions of the pregnant solution.

the alcoholic α-protons. Results for the different compositions of the organic solvent were given in Table I. Such a remarkable shift of the amine α-proton resonance from 2.3 to 3.5 ppm is a strong evidence of formation of ammonium tungstate, although the molecular form of the tungstate is not known. Similar phenomenon was observed in the polyamines.[13] Disappearance of the fine structure of the amine α-proton peak in the loaded solvent indicates probably the rigidity of N-C bonds of the ammonium ion, R_3NH^+, when it is fixed as an ammonium tungstate salt. Tungsten is present as many different forms of oxytungstate ions in the aqueous solution depending on its pH[14-15]. Meta-tungstate is the predominant form in the acidic range ($pH\sim2$). Therefore, it may be assumed that tungsten is extracted

Table I. Chemical shifts of the organic solvents at each loading step.

Solvent	Number of extractions	NOA		TOA
		—OH	—CH$_2$—O—	N$\begin{smallmatrix}/\text{CH}_2-\\-\text{CH}_2-\\\backslash\text{CH}_2-\end{smallmatrix}$
TOA 5 %	0	—	—	2.36
in n-C$_6$H$_{14}$	1	—	—	2.92
TOA 5 %	0	2.82	3.56	2.39
NOA 3 %	5	( )*	3.62	3.34
in n-C$_6$H$_{14}$	8	3.16	3.62	3.40
TOA 5 %	0	4.16	3.55	2.37
NOA 10 %	1	4.42	3.58	3.16
in n-C$_6$H$_{14}$	5	3.88	3.58	3.40
	6	3.76	3.59	3.44
	7	3.78	3.59	3.44
	8	3.76	3.58	3.44
TOA 5 %	0	4.48	3.55	2.37
NOA 15 %	1	4.42	3.58	3.20
in n-C$_6$H$_{14}$	5	4.12	3.57	3.40
	6	4.08	3.58	3.40
	8	4.08	3.58	3.40

* Overlapped with the alcoholic α-proton peak.

into the organic phase as ammonium metatungstate, $(R_3NH)_6H_2W_{12}O_{40}$. Thus our discussion will be confined to the interaction of alcohol with trioctyl ammonium metatungstate to understand its synergistic effect.

It has been seen in Fig. 5 that the broad alcoholic proton band (δ=5.0 ppm) of the acidified solvent was moving to up-field with sharper band width as extraction continued. This is probably due to fixation of the ammonium ion and release molecule from the range of its interaction with the ammonium ion. The ammonium proton seems not allowed to exchange with the alcoholic proton. However, at maximum loading the alcoholic proton resonance appeared finally as a sharp singlet instead of a triplet. This means that the alcohol molecule is still interacting in some way but not with the ammonium ion. Thus the most feasible molecular

interaction is via hydrogen bonding between alcohol and tungstate ion. We can imagine two possible ways of hydrogen bonding since the polymeric tungstate ion has both hydroxy and oxygen sites. However, since in the metatungstate form, $W_{12}O_{38}(OH)_2^{6-}$, two hydrogen atoms are caged in the central tetrahedral cavity of the Keggin[6] structure, the two hydroxy groups can not participate in the hydrogen bonding with alcohol. Therefore, the only possible form of hydrogen bonding would be the following:

Polymer $\quad$ W=O $\cdots$ H-O-R
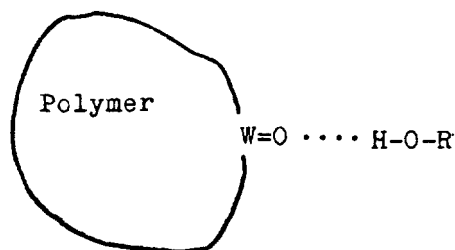
Such hydrogen bonding is expected to be relatively weak compared with that between organic molecules. Nevertheless, since one polymeric tungstate ion has many oxygen sites, such surrounding hydrogen bonding may stabilize the large molecule and increase its solubility in the hydrocarbon medium.

An alternative explanation of the synergistic effect of alcohol might be sought via a quite different mechanism which could be experimentally tested. The solubility increase of the ammonium tungstate in the organic solvent could be due to the increase of its dielectric constant by addition of NOA. The dielectric constant is calculated to be $\epsilon \sim 1.9$ for the organic solvent composed of 5 % TOA and 95 % n-hexane, but increased to 2.6 when 5 % NOA is added as shown in *Table* II. If the solubility increase is simply ascribed to molecular dipole-dipole interaction between the tungstate and alcohol, some other material with high dielectric constant may replace alcohol as phase conditioner. Nitrobenzene seems to be a suitable one in this respect. Addition of 3 % nitrobenzene to the 5 % TOA solvent raised the dielectric constant ($\epsilon = 3.12$) higher than that of 5 % TOA-5 % NOA solvent. However, nitrobenzene did not affect the solubility of the tungstate, and gelatine was formed

when the 5 % TOA-3 % NB solvent was shaken with the third portion of the pregnant solution whereas the 5 % TOA-5 % NOA solvent did not yield gelatine even after 10th portion of the pregnant solution as was mentioned earlier. Increasing nitrobenzene concentration resulted in the same. Thus the mechanism of dipole-dipole interaction may be excluded.

After all, we believe the hydrogen bonding between alcohol and the polytungstate ion is the best model for the synergistic role of alcohol in the amine solvent extraction.

Acknowledgement

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Table II. Effect of dielectric constants of the solvents to the loading capacity.

Comositions of Solvents	Dielectric Constant	Number of Extractions	Remark
TOA 5 % n-C$_6$H$_{14}$ 95 %	1.9	3	gel
TOA 5 % NOA 5 % n-C$_6$H$_{14}$ 90 %	2.6	>10	no gel
TOA 5 % C$_6$H$_5$NO$_2$ 3 % n-C$_6$H$_{14}$ 92 %	3.12	3	gel
TOA 5 % C$_6$H$_5$NO$_2$ 5 % n-C$_6$H$_{14}$ 90 %	5.96	3	gel

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