다중텅그스텐산 아민염의 분자량 측정

卞 鍾 洪 · 蓮 孫 秀

한 국 과 학 기 술 연 구 소

(1974. 2. 18 접수)

Cryoscopy of Amine-Polytungstates

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(Received Feb. 18, 1974)

요 약. 비수용성 긴고리 지방족 아민인 $(n\text{-}C_8H_{17})_3N$과 $(n\text{-}C_8H_{17})_3NCH_3Cl$을 사용하여 산도가 틀린 텅그스텐산수용액 (pH=2, 4, 6)으로 부터 용매추출법에 의하여 유기용매에 녹는 다중텅그스텐산 아민염을 제조하는데 성공하였다. 제조된 텅그스텐산 아민염의 분자량을 벤젠용매에서 더미스터를 이용한 감도 1/4000 °C의 휘트스톤 브리지를 사용하여 측정할수 있었다. 분자량 측정결과와 화학분석 및 적외선 스펙트럼으로 부터 pH=2, 4에서 생긴 아민염은 메타텅그스텐산염, pH=6에서 생긴 아민염은 파라텅고스텐산염이 아니고 미지의 새로운 다중텅고스텐산염임을 알수 있었다.

Abstract. Trioctylamine- and tricaprylylmethylammonium chloride-tungstate salts have been prepared by solvent extraction from the sodium tungstate solution of various acidities (pH=2, 4, 6). The molecular weights of the amine-tungstate salts thus obtained could be cryoscopically measured in benzene by means of a home-built Wheatstone bridge utilizing thermistor with sensitivity of 1/4000 °C. The cryoscopic data along with the results of chemical analysis and infrared spectra of the salts indicate that the amine-tungstates prepared at pH=2 and 4 are all metatungstate whereas the salt obtained at pH=6 is an unknown form quite different from the expected paratungstate.

Introduction

The orthotungstate ion $WO_4{}^{2-}$ is known to undergo polymerization at low pH to form higher molecular weight isopolyanions. Many different form of polymeric anions were claimed to exist in solution by several workers[1,2], but only a few of them were isolated and identified. para-, ψ-meta- and meta-tungstates are known to exist both in solid and solution, but their exact molecular forms are still on debate except for the meta-form which was found to be same as the Keggin structure[3].

Of many physico-chemical methods cryoscopy is one of the most powerful tools to measure the degree of polymerization. The freezing point depression of sodium polytungstates in aqueous solution is not sensitive to change in the degree of tungstate condensation. For such a reason a sedimentation method was attempted[1]. However, the cryoscopy of polytungstate salts in neutral state in organic solvent seems to be most valid, but it offers two experimen-

tal difficulties: Most polytungstate salts either of alkali or organic cations are insoluble in organic solvent, and atmospheric moisture may be contaminated to cause a serious error when their molecular weight is measured by an ordinary cryoscopic method, since the molecular weihgts of tungstates are very large.

We have succeeded in isolation of soluble amine-tungstates using long chain aliphatic amines, and their molecular weights could be cryoscopically measured by means of a specially built Wheatstone bridge utilizing thermistor. In this report we present the details of the measuring apparatus and the cryoscopic data of the isolated amine-polytungstates.

Experimental

Preparation of Amine-Polytungstates. Amine-tungstate salts were prepared by repeated solvent extraction as described in our previous report[4]. An organic phase containing 10% amine in n-hexane(100 ml) was shaken in a separatory funnel with 100 ml of $0.1 M$ Na_2-WO_4 aqueous solution adjusted to a desired acidity(pH=2,4,6). After the two phases were separated, the aqueous layer was drained off and a new portion of the sodium tungstate solution was replaced to shake again with the partly loaded organic phase. The same process was repeated until the gelatinous amine-tungstate precipitated out, which was washed both with water and n-henane and then purified twice by employing a benzene-hexane solvent pair. Final purification was performed by using dried benzene and hexane[5].

Cryoscopic Measurements. The freezing temperatures of amine-tungste solutions in benzene have been measured by means of a Wheatstone bridge including a thermistor as shown in *Fig.* 1A. The resistance of a thermistor is related to the temperature by the following equation[6]:
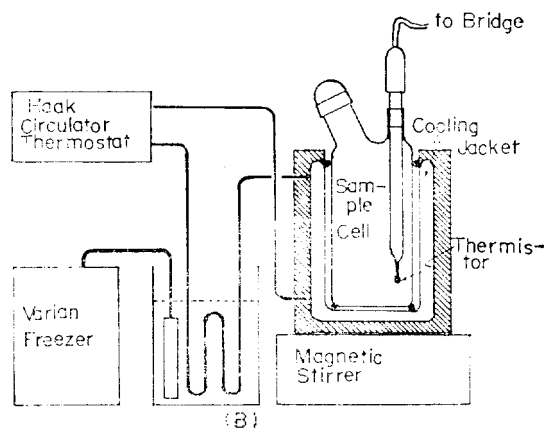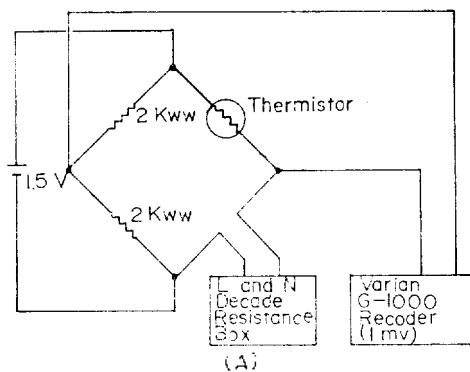

*Fig.*1. Apparatus for cryoscopic measurement

$$R = A \exp(B/T)$$

where A and B are constants characteristic of the thermistor and T is its absolute temperature. It is seen from the above equation that within a narrow temperature range, the change of the thermistor resistance may be given by

$$\Delta R/R = -B \cdot \Delta T/T^2$$

Hence, around the freezing temperature of a specific solvent, the resistance increment ΔR may be related to molality as in the following:

$$\Delta R = (-BR/T^2)K_f \cdot m = K'_f \cdot m$$

Therefore, if the K'_f value for a particular set of solvent and thermistor is determined from a measured standard curve, the molecular weight of the unknown can be obtained from the measured resistance increment of its solution.

In this experiment the K'_f value for the set of benzene and the thermistor specified in the following has been determined to be $7.59\,\Omega/10^{-4}$ mole by use of ferrocene, naphthalene and anthracene as standrd materials.

The thermistor used is a glass-sealed bead type GB32J2 from Fenwel Electronics and its resistance is $2000\,\Omega\pm20\,\%$ at 25 °C with a temperature coefficient of $-3.9\,\%/°C$. Since the bead type thermistor shows a fast response and has a large temperature coefficient, its Wheatstone bridge allows a measurement of temperature change down to 1/2000 °C. As a detector Varian G1000 strip chart recorder was used and a division (0.01 mv) of the chart paper was equivalent to a temperature change of 1/4000 °C.

The sample cell and its temperature control unit are shown in Fig. 1B. The sample cell is separable from the cooling jacket which is kept at 2±0.02°C by using a Haak circulator and a Varian freezer. It is important to keep the cooling jacket at the constant temperature in order to obtain reproducible results. The sample cell with inner diameter of 22 mm is all ground-jointed so that its inner compartment may become air-tight.

An appropriate amount of a sample was weighed in the cell and then 15 ml benzene was added. After complete dissolution, the air-sealed cell was put into the cooling jacket to measure its freezing point. The whole sampling procedure was carried out under throughly dried atmosphere using a dry box.

In general, when the Beckman thermometer is used, the cooling curve of a solution is represented as shown in Fig. 2A. In this case the point P extrapolated from the straight part cd is taken as its freezing point. However, such an extrapolation is almost impossible in case the thermistor is employed (Fig. 2B), since no straight part cd is observed because of its high

sensitvity. Instead, when the minmum supercooled points T_{sc} were plotted against the maxmum temperatures T_{max}, a linear relationship was observed as is seen in Fig. 2C. The extrapolated point T_i in this curve is the zero-supercooling temperature which is the true freezing point of the solution. It should be noticed that the above-mentioned cryoscopic method utilizing thermistor is specially suitable not only for high molecular weight compounds but also for
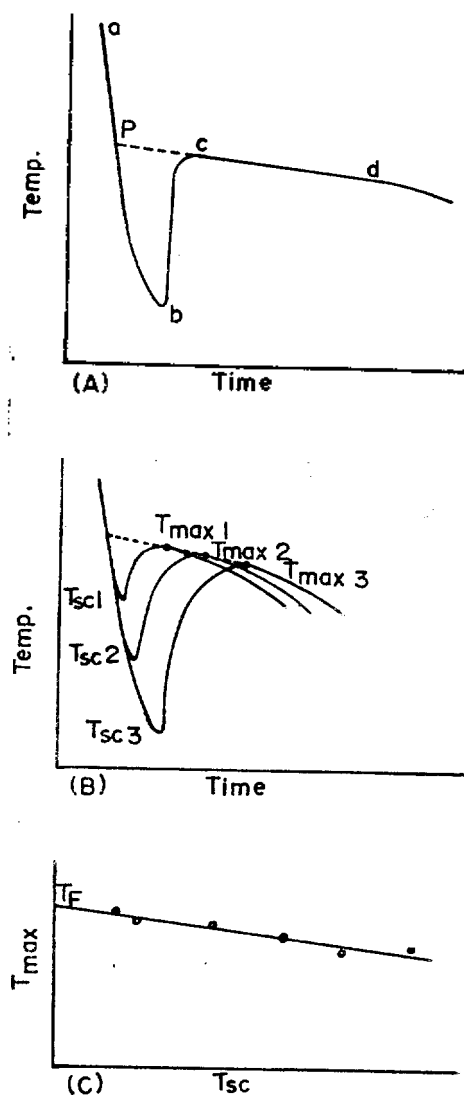

Fig. 2. Cooling curves.

air-and/or moisture-sensitive complexes.

Results and Discussion

Preparation of various amine-tungstates was attempted by directly mixing the acidified solution of sodium tungstate with an aqueous solution of aryl or short chain aliphatic amine at the same acidity. Condensation of the mixed solution by slow evaporation resulted in crystalline salts but they were all insoluble in organic solvents and as such not suitable for cryoscopic measurement. However, it has been found that some water-insoluble long chain aliphatic amines could be used to prepare soluble amine-tungstates by employing the solvent extraction technique. The amines selected for this purpose are trioctyl amine(TOA), $(n-C_8-H_{17})_3N$ and tricaprylylmethyl ammonium chloride(TCMAC), $(n-C_8H_{17})_3NCH_3Cl$.

When the amine-containing organic phase was contacted with the aqueous tungstate solution, an amine-tungstate was found to be formed by ion exchange mechanism and the resultant salt was loaded into the organic phase. Consequently the use of an organic solvent(n-hexane) with low loading capacity allowed the isolation of a gelatinous amine-tungstate salt from both phases because it is also insoluble in aqueous phase. Thus several TOA-and TCMAC-tungstates were prepared from different sodium tungstate solutions of various acidities(pH=2, 4, 6). TCMAC-tungstate could be made at any acidity while the preparation of TOA-tungstate was successful only at pH=2. TOA- and TCMAC-tungstates thus obtained are all soluble in benzene and other polar organic solvents.

Preparation of such soluble polytungstate salts bears an important significance in that polymeric tungstate ions can be studied in isolated state and their molecular structure as well as their polymeric nature may be elucidated from measurements of their physical properties in

organic solvents.

The results of the cryoscopic measurements in benzene and chemical analysis data of the salts are given in *Table* 1.

In order to characterize those amine-tungstates based upon the data obtained it is necessary to examine briefly the results of studies by other workers. There are remarkable discrepancies in claiming the molecular species, formulations and structures of polytungstate ions among several authors. According to Emeleus and Anderson[7], for example, at pH=6 WO_4^{2-} ion polymerizes to paratungstate A and then partly transforms to paratungstate B to be in equilibrium, which were formulated as $(HW_6-O_{21})^{5-}$ and $(H_{10}W_{12}O_{46})^{10-}$, respectively. In more acidic solution(pH≃4) ψ-metatungstate being formulated to $(H_3W_6O_{21})^{3-}$ is formed and it may be transformed to metatungstate $[H_2(W_3-O_{10})_4]^{6-}$. Glemser[1] proposed a similar but more detailed scheme, which however shows considerable differences in molecular formulations. In particular, contrary to the former, his para-A, para-B, ψ-meta and meta-forms were represented as $(W_6O_{20}(OH))^{5-}$ $(W_{12}O_{36}(OH)_{10})^{10-}$, $(W_{24}O_{72}(OH)_{12})^{12-}$ and $(W_{12}O_{38}(OH)_2)^{6-}$, respectively.

Several other forms, for example, ditungstate $W_2O_7^{2-}$,[8~10] tritungstate $W_3O_{10}^{2-}$,[11] tetratungstate $W_4O_{13}^{2-}$,[9,11] and pentatungsttae $W_5O_{16}^{2-}$[11] were claimed under different experimental conditions, but only the para- and meta-forms were relatively well characterized. Therefore, we tentatively assume only these forms for the amine-tungstates obtained and the theoretical values of their molecular weights and compositions are given in *Table* 2. It is important to point out that the chemical compositions sharply distinguish between the para- and meta-tungstates while the para-A and B forms(as well as the meta- and ψ-meta-forms) are clearly distinguished from each other by their molecular

Table 1. Cryoscopic and chemical analysis data of TOA-and TCMAC-tungstates

Compounds	Mol. wt.	C	H	WO$_3$
TOA(n-C$_8$H$_{17}$)$_3$N	357			
TCMAC, (n-C$_8$H$_{17}$)$_3$NCH$_3$Cl	526			
TOA-tungstate at pH=2	4,700			
TCMAC-tungstate at pH=2	5,440	34.8	6.7	53.67
TCMAC-tungstate at pH=4	5,530	36.8	6.9	53.82
TCMAC-tungstate at pH=6	10,600	37.9	6.7	52.72

Table 2. Calculated molecular weight and chemical composition for some possible molecular forms of amine-tungstate

Possible formula	Mol. wt.	C	H	WO$_3$
TOA, Para-A, [(C$_8$H$_{17}$)$_3$NH]$_5$ [W$_6$O$_{20}$(OH)]	3,207.5	44.9	8.01	43.57
Para-B, [(C$_8$H$_{17}$)$_3$NH]$_{10}$ (W$_{12}$O$_{36}$(OH)$_{10}$)	6,479.0	44.5	7.93	42.94
Meta, [(C$_8$H$_{17}$)$_3$NH]$_6$ [W$_{12}$O$_{39}$(OH)$_2$]	4,968.3	34.8	6.21	56.00
ψ-Meta, [(C$_8$H$_{17}$)$_3$NH]$_{12}$ [W$_{24}$O$_{72}$(OH)$_{12}$]	10,000.5	34.6	6.27	55.64
TCMAC, Para-A, [(C$_8$H$_{17}$)$_3$NCH$_3$]$_5$ (W$_6$O$_{20}$(OH)]	3,283.7	45.7	8.32	42.36
Para-B, [(C$_8$H$_{17}$)$_3$NCH$_3$]$_{10}$(W$_{12}$O$_{36}$(OH)$_{10}$)	6,639.4	45.2	8.35	41.91
Meta, [(C$_8$H$_{17}$)$_3$NCH$_3$]$_6$ [W$_{12}$O$_{39}$(OH)$_2$]	5,060.4	35.6	6.49	54.98
ψ-Meta, [(C$_8$H$_{17}$)$_3$NCH$_3$]$_{12}$[W$_{24}$O$_{72}$(OH)$_{12}$]	10,193.0	35.4	6.53	54.59

weights. It is easily seen from comparison with the experimental values(Table 1) that the TOA- and TCMAC-tungstates prepared at pH=2 and 4 may be all identically meta-form whereas the TCMAC-tungstate at pH=6 may possibly be ψ-meta-form. However, some other spectral data are necessary for further confirmation, since the possibility of some other unkown form can not be excluded. As a matter of fact, the latter seems to be the case. The Infrared spectra of TOA- and TCMAC-tungstates are shown in Fig. 3 and compared with those of the potassium salts given by Glemser. For simplicity only the part of W—O stretching region was given. Although the comparison is not clear because of poor resolution of Glemser's spectra, spectra, it is certain that the amine salts at pH=2 and 4 shows the same pattern of W—O stretching as the potassium metatungstate.

However, the amine salt at pH=6 presents considerably different W—O stretching modes from the potassium ψ-metatungstate. This means the latter may be a new unkown form of polytungstate resembling the ψ-meta-tungstate in chemical composition and molecular weight. However, such a conclusion is not necessarily contrary to the results by other workers asserting that Para-forms are are mjor species in the tungstate solution at pH=6, because the amine may have a favored selectivity over a specific form of the polytungstate ions. In fact, it has been found in a separate experiment that contrary to the case of TCMAC some primary amines combine selectively with a paratungstate ion at the same pH. The resulrs of more detailed studies on this subject including the exact molecular form of the unknown and other prorerties of amine-polytung-
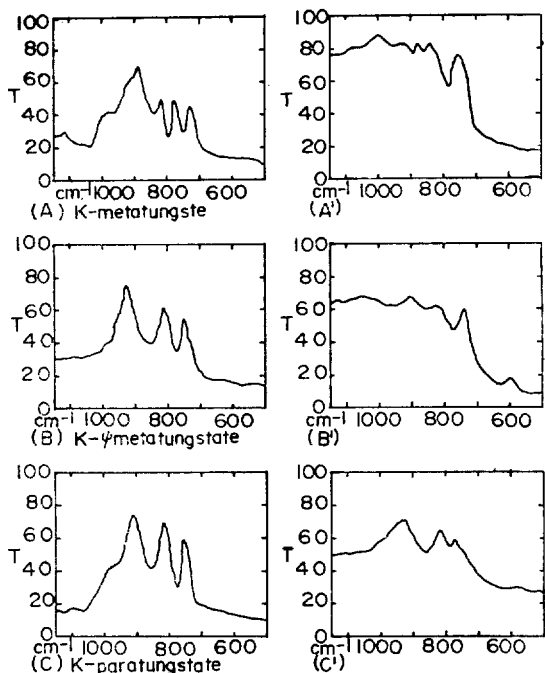
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Fig. 3. IR spectra of isopolytungstates
(*A*), (*B*), (*C*) : Glemser's spectra
(*A'*), (*B'*), (*C'*) : Spectra of TCMAC-tungstates at pH=2, 4, 6 respectively

states will be fully reported in the succeeding papers.

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