

Research on synergistic extraction of rhenium(VII) from hydrochloric media by mixtures of tri-alkylamine and tri-n-butylphosphate

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Abstract: The synergistic extraction of Re(VII) from hydrochloric media by mixtures of tri-alkylamine (N235) and tri-n-butylphosphate (TBP) is studied. The mixtures have higher synergistic effects on Re(VII) than that on Mo(VI), and the maximal synergistic factors of the mixture for Re(VII) and Mo(VI) are 4.71 and 2.16 at a concentration ratio of N235 to TBP of 1 to 9. Re(VII) is extracted as $(R_3NH^+ Cl^-)_2 \cdot HReO_4 \cdot B$ at $pH = 1$, whereas Re(VII) is extracted as $(R_3NH^+ Cl^-) \cdot HReO_4 \cdot B$ by the mixtures at the acidity of $3 \text{ mol} \cdot L^{-1}$, instead of $R_3NH^+ ReO_4^-$ by N235 alone. Furthermore, the possibility of separating rhenium and molybdenum ions by the mixtures according to the synergistic effects and extraction ability are proved.

Key words: synergistic extraction; tri-alkylamine; tri-n-butylphosphate; rhenium; molybdenum

0 Introduction

Rhenium is mainly found in pegmatites, rocks altered by pneumatolysis, and especially in molybdenites associated with copper recovered through roasting or direct reduction of the concentrates^[1]. Among the recovery methods of rhenium, extraction is a widely studied method^[2-3]. The main source of rhenium is the processing of flue-dust collected during the molybdenite roasting operation, so the separation of rhenium from molybdenum in aqueous solution is difficult because of their similar chemical behavior, which has always been a problem in hydrometallurgy^[4-5]. It is important to explore some new extraction systems or separation methods superior to the current extraction process which has been widely

applied to recovery of rhenium^[6-8].

Synergistic effect, as a universal phenomenon in solvent extraction, has been studied extensively^[9-14]. In particular, the advantages of Re(VII) extraction by a synergistic mixture of tertiary amine and tributylphosphate have been examined^[15]. Although amines or quaternary ammonium salts are common reagents used to extract and separate Re(VII) and Mo(VI) in practice, it is widely recognized that their mutual separation needs to be improved. So it is important to investigate new systems involving tertiary amine as an extractant to extract Re(VII), using neutral organophosphorus reagents as synergists, with a view toward developing new systems to separate Re(VII) and Mo(VI) according to the synergistic or antagonistic effects. In the present work, the

Received by: 2018-10-15; Revised by: 2019-05-20.

Supported by: National Natural Science Foundation of China (21171080, 21201094).

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extraction of Re(VII) from Mo(VI) by mixtures of tri-alkylamine (N235, abbreviated as R_3N) and tri-n-butylphosphate (TBP, abbreviated as B) will be studied.

1 Experiments

1.1 Reagents

Tri-alkylamine (N235, R_3N , $R = C_8-C_{10}$) was kindly supplied by Shanghai Institute of Organic Chemical. Tri-n-butylphosphate (TBP) was kindly supplied by Tianjin Chemical Reagent No. 1 Plant. All the reagents were used without further purification. NH_4ReO_4 (99.9%) and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (99.9%) were used to prepare rhenium and molybdenum stock solutions.

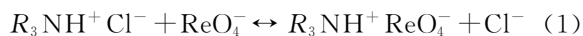
1.2 Procedure

N235 was pre-equilibrated with the same volume of 3 mol/L HCl solution in the absence of the metal ions, and then was separated and washed with distilled water until neutral pH for the following experiment. For the equilibrium experiments, equal volumes of aqueous phase (5 mL) and organic phase (5 mL) were mixed and shaken for 30 min at (298 ± 1) K, which were sufficient for equilibrium attainment. After phase separation, the concentration of Re(VII) and Mo(VI) in the aqueous phase was determined by 7230 Model Grating Spectrophotometer and PEAA 700 Atomic Absorption spectrophotometer, respectively. The concentration of metal ions in the organic phase was determined by mass balance analysis. The distribution ratio D was taken as the ratio of the concentration of metal ion in the organic phase to that in the aqueous phase.

2 Results and discussion

2.1 Extraction of Re(VII) with N235 or TBP

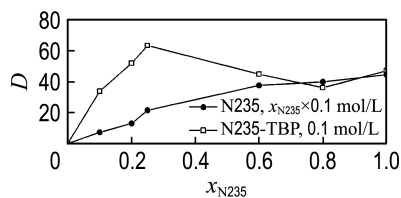
The extraction of Re(VII) with N235 from $(H, NH_4)Cl$ solutions has been reported earlier^[8]. The extraction mechanism of Re(VII) using N235 is shown as



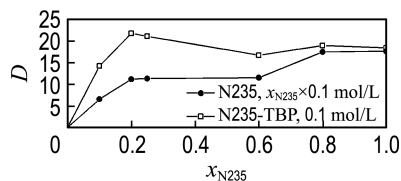
TBP is a neutral organophosphorus extractant. At these experimental conditions, the result shows that the extraction effect of Re(VII) with TBP alone is negligibly small. Although the extraction of rhenium in hydrochloric acid media has been reported in some references^[12-13], TBP alone is not able to extract rhenium due to low concentration of hydrochloric acid at experimental conditions of this paper. Thus, the value of D_{TBP} at these experimental conditions is regarded as 0.

2.2 Synergistic effect of Re(VII) and Mo(VI) with the mixtures of N235 and TBP

Fig. 1 shows the extraction of Re(VII) or Mo(VI) from chloride media with the mixtures of N235 and TBP in heptane, where x_{N235} represents molar fraction of N235 in the solution, and μ represents ionic strength of solution. The synergistic enhancement factors, $r = D_{N235-TBP} / (D_{N235} + D_{TBP})$, are listed in Tab. 1. The value of r indicates that the extraction has synergistic effect ($r > 1$) and antagonistic effect ($r < 1$). It is obvious that it shows more evident synergistic effect on the extraction of Re(VII) than that of Mo(VI) with the mixtures of N235 and TBP when $c_{N235} = 0.010-0.025$ mol/L. Moreover, at concentration ratio of N235 to TBP of 1 to 9, the maximal synergistic



(a) Re(VII), 5×10^{-4} mol/L



(b) Mo(VI), 5×10^{-2} mol/L

Fig. 1 Extraction of metal ions by N235 alone or mixtures of N235 and TBP from Re(VII) or Mo(VI) solution ($c(H^+) = 0.1$ mol/L, $\mu = 0.1$ mol/L)

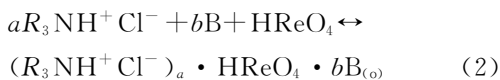
Tab. 1 Synergistic enhancement factors of Re(VII) and Mo(VI) with the mixtures of N235 and TBP

$c_{\text{N235}}/(\text{mol} \cdot \text{L}^{-1})$	$c_{\text{TBP}}/(\text{mol} \cdot \text{L}^{-1})$	r_{Re}	r_{Mo}
0	0.100	1.00	1.00
0.010	0.090	4.71	2.16
0.020	0.080	4.01	1.94
0.025	0.075	2.95	1.86
0.060	0.040	1.20	1.45
0.080	0.020	0.93	1.08
0.100	0	1.00	1.00

enhancement factor could be obtained as 4.71 for Re(VII) and 2.16 for Mo(VI). This phenomenon of synergistic effect can be explained as that TBP is a nucleophilic (protic) reagent, which solvates an amine salt cation thus enhances its extracting ability^[16-17].

2.3 Extraction mechanism of Re(VII) with mixtures of N235 and TBP

Firstly, the effects of concentration of Cl^- on the extraction of Re(VII) by the mixtures have been studied. It is found that they are independent of each other, which means the species of Cl^- do not participate in the synergistic extraction reaction^[8]. Thus, the synergistic extraction equation of Re(VII) with the mixtures of N235 and TBP is expressed as

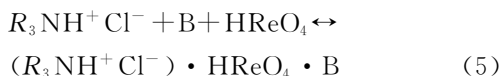
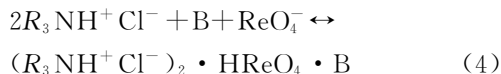


where a and b represent unknown coefficients, then the distribution ratio ($D_{\text{N235-TBP}}$) of the synergistic extraction system should be

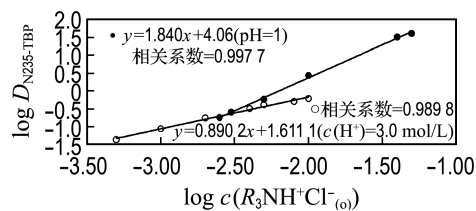
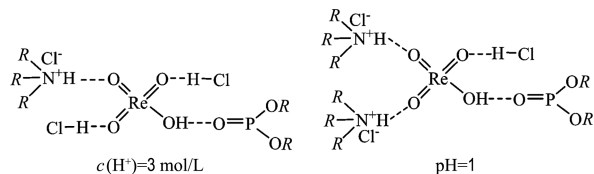
$$\log D_{\text{N235-TBP}} = \log K + a \log c(\text{R}_3\text{NH}^+\text{Cl}^-_{(\text{o})}) + b \log c(\text{B}_{(\text{o})}) \quad (3)$$

To examine the composition of extracted complexes in the N235 and TBP system, the distribution ratio $D_{\text{N235-TBP}}$ is determined at a fixed concentration of N235 or TBP. Plots of $\log D_{\text{N235-TBP}}$ versus $\log c(\text{R}_3\text{NH}^+\text{Cl}^-_{(\text{o})})$ at a fixed concentration of TBP give straight lines with slopes of about 2.0 at $\text{pH} = 1$ and 1.0 at $c(\text{H}^+) = 3.0 \text{ mol/L}$, whereas the slopes for $\log D_{\text{N235-TBP}}$ versus $\log c(\text{B}_{(\text{o})})$ at a fixed concentration of N235 are both about 1.0 at the different acid concentrations, as shown in

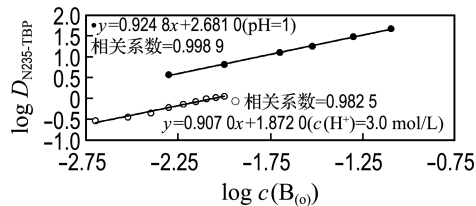
Fig. 2(a) and (b). It is inferred that the mechanism of extraction reaction is that the number of TBP participating in extraction reaction is more at high acidity ($c(\text{H}^+) = 3.0 \text{ mol/L}$), while the number of TBP participating in extraction reaction is less at low acidity ($\text{pH} = 1$), so more N235 can be bound with ReO_4^- . The synergistic extraction reaction can be described by Eqs. (4) and (5), respectively.



Re(VII) is extracted as $(\text{R}_3\text{NH}^+\text{Cl}^-)_2 \cdot \text{HReO}_4 \cdot \text{B}$ at $\text{pH} = 1$, whereas Re(VII) is extracted as $(\text{R}_3\text{NH}^+\text{Cl}^-) \cdot \text{HReO}_4 \cdot \text{B}$ by the mixtures at $c(\text{H}^+) = 3.0 \text{ mol/L}$, instead of $\text{R}_3\text{NH}^+\text{ReO}_4^-$ by N235 alone. The chemical structural formulas are as follows:



(a) N235, 0.01 mol/L



(b) TBP, 0.01 mol/L

Fig. 2 Relationship between distribution ratio $D_{\text{N235-TBP}}$ and equilibrium concentration of TBP and N235 ($c(\text{Re(VII)}) = 5 \times 10^{-4} \text{ mol/L}$)

2.4 Separation of Re(VII) and Mo(VI) with mixtures of N235 and TBP

The separation factor ($\beta_{\text{Mo/Re}}$), as one of the

most common parameters of evaluating the separation abilities, is the distribution ratio of two metals measured under the same condition. Hence, the $\beta_{\text{Mo/Re}}$ can be defined as $D_{\text{Mo}}/D_{\text{Re}}$. The separation factors $\beta_{\text{Mo/Re}}$ obtained at different concentration ratios of N235 and TBP are given in Tab. 2. It demonstrates that the separation factors ($\beta_{\text{Mo/Re}}$) are really high at the range of the concentration ratio of N235 and TBP in the mixtures from 1 : 1 to 1 : 1.5 at pH 2, and

higher than that in N235 alone system (21.11). When the concentration ratio of N235 and TBP in the mixtures is 1 : 1, it is clear that the mixtures have effective separation ability for rhenium and molybdenum ($\beta_{\text{Mo/Re}} = 45.44$) and also higher extraction ability for them ($D_{\text{Re}} = 5.62$, $D_{\text{Mo}} = 255.20$). It means that Re(VII) and Mo(VI) can be extracted and separated if a proper ratio of the two extractants is used.

Tab. 2 Separation factors $\beta_{\text{Mo/Re}}$ by using mixtures of N235 and TBP ($c(\text{Re(VII)}) = 5 \times 10^{-4}$ mol/L, $c(\text{Mo(VI)}) = 5 \times 10^{-2}$ mol/L, $\mu = 0.1$ mol/L, $c(\text{N235}) + c(\text{TBP}) = 0.2$ mol/L)

Acid concentration of aqueous phase	$n(\text{N235}) : n(\text{TBP}) = 1 : 0$			$n(\text{N235}) : n(\text{TBP}) = 1 : 1$			$n(\text{N235}) : n(\text{TBP}) = 1 : 1.5$		
	D_{Re}	D_{Mo}	$\beta_{\text{Mo/Re}}$	D_{Re}	D_{Mo}	$\beta_{\text{Mo/Re}}$	D_{Re}	D_{Mo}	$\beta_{\text{Mo/Re}}$
pH=10	5.45	0	0	1.43	1.36	0.95	0.59	0.48	0.82
pH=5	14.11	1.00	0.07	2.33	0.90	0.39	1.27	0.81	0.64
pH=2	13.38	282.44	21.11	5.62	255.20	45.44	3.16	141.33	44.67
pH=1	1.98	33.00	16.67	2.78	21.67	7.79	12.13	16.49	1.36
3 mol/L	0.81	0.01	0.02	0.83	0	0	0.82	0.02	0.03

Acid concentration of aqueous phase	$n(\text{N235}) : n(\text{TBP}) = 1 : 4$			$n(\text{N235}) : n(\text{TBP}) = 1 : 9$			$n(\text{N235}) : n(\text{TBP}) = 1 : 19$		
	D_{Re}	D_{Mo}	$\beta_{\text{Mo/Re}}$	D_{Re}	D_{Mo}	$\beta_{\text{Mo/Re}}$	D_{Re}	D_{Mo}	$\beta_{\text{Mo/Re}}$
pH=10	0.14	0.09	0.66	0.10	0.06	0.61	0.01	0.02	1.91
pH=5	0.23	0.69	2.97	0.11	0.69	6.10	0.13	0.67	5.24
pH=2	0.67	6.54	9.75	0.37	3.36	9.05	0.12	2.66	22.24
pH=1	8.63	6.16	0.71	22.48	3.65	0.16	1.61	2.69	1.67
3 mol/L	0.58	0	0.01	0.52	0	0	0.25	0.07	0.27

3 Conclusions

Mixtures of tri-alkylamine (N235) and tri-n-butylphosphate (TBP) exhibit evident synergistic effects when they are used to extract Re(VII) from Mo(VI) in chloride media. The stoichiometries of the extracted complexes with the synergistic mixtures have been determined by numerical methods to be $(\text{R}_3\text{NH}^+ \text{Cl}^-)_2 \cdot \text{HReO}_4 \cdot \text{B}$ at pH = 1 and $(\text{R}_3\text{NH}^+ \text{Cl}^-) \cdot \text{HReO}_4 \cdot \text{B}$ at $c(\text{H}^+) = 3.0$ mol/L, respectively. It is feasible and advantageous to separate Re(VII) from Mo(VI) at the concentration ratio of N235 and TBP in the mixtures from 1 : 1 to 1 : 1.5 at pH 2 because of large enough $\beta_{\text{Mo/Re}}$, and then to extract Re(VII) at concentration ratio of N235 to TBP of 1 to 9 due to large synergistic enhancement factor $r(4.71)$. The N235-TBP synergistic extraction system can effectively

extract molybdenum and rhenium, respectively.

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三烷基胺和磷酸三丁酯于盐酸介质中协同萃取铼(VII)研究

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摘要: 研究了三烷基胺(N235)和磷酸三丁酯(TBP)从盐酸介质中对铼的协同萃取。N235和TBP的浓度比为1:9时混合萃取体系对Re(VII)具有较大的协萃作用,最大协萃因子为4.71,对Mo(VI)的协萃因子为2.16。在pH=1时,萃合物的组成为 $(R_3NH^+Cl^-)_2 \cdot HReO_4 \cdot B$,当酸浓度为 $3 \text{ mol} \cdot L^{-1}$ 时,萃合物的组成为 $(R_3NH^+Cl^-) \cdot HReO_4 \cdot B$,而N235单独萃取时萃合物的组成为 $R_3NH^+ReO_4^-$ 。同时证明了混合萃取剂分离钼和铼的协萃效果和萃取能力。

关键词: 协同萃取;三烷基胺;磷酸三丁酯;铼;钼

中图分类号: O653.62

文献标识码: A

doi: 10.7511/dllgxb201904001

收稿日期: 2018-10-15; 修回日期: 2019-05-20.

基金项目: 国家自然科学基金资助项目(21171080,21201094).

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