THE EFFECT OF SULPHURIC ACID CONCENTRATION ON SOLVENT EXTRACTION OF ReO$_4^-$ BY THE LONG-CHAIN ALIPHATIC TERTIARY AMINES AND ALCOHOLS

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Abstract: The effect of sulphuric acid concentration on solvent extraction of ReO$_4^-$ by the long-chain aliphatic tertiary amines and alcohols in a wide range of H$_2$SO$_4$ concentrations in initial solutions is discussed. It has been established that the influence of the sulphuric acid concentration on rhenium solvent extraction is largely due to the extraction process mechanism. In the case of the anion-exchange mechanism, ReO$_4^-$ is best extracted from weakly acidic solutions, whereas when the hydrate-solvate mechanism takes place – from solutions containing 4-7 mole/l H$_2$SO$_4$.

Keywords: Rhenium, solvent extraction, long-chain aliphatic tertiary amine and alcohols, sulphuric acid media.

Introduction

Rhenium is one of the rarest trace metals. The rhenium clark is $7 \cdot 10^{-8}$ %; rhenium compounds commonly occur in nature as an isomorphous impurity in molybdenite, in sulfide copper ores and, still rarer, in polymetallic ores.

Depending on the kind of raw material and equipment used, pyrometallurgical processing of rhenium-bearing concentrates can yield up to 96% of rhenium sublimated to the gaseous phase, next captured and concentrated in the wet scrubbing system. Wet scrubbing sulfuric solutions (wash sulphuric acid) from copper and copper-molybdenum plants is the main industrial source of the metal and may contain 60 to 700 g/l H$_2$SO$_4$ and more, and up to 1.5 g/l rhenium. Up to date, rhenium has been recovered from such solutions by solvent extraction technologies with tertiary amine-type extragents [1-3].

The extraction of rhenium by tertiary amines has been extensively described in the literature. However, the available data on the impact of acidity are fairly contradictory [1-7]. Knowing that acidity is a major factor controlling the process efficiency, we undertook studying the effect of H$_2$SO$_4$ concentration on rhenium distribution coefficients during the extraction by tertiary amines and high-molecular aliphatic alcohols usually employed as a modifier in tertiary-amine based extraction mixtures.

Experimental

In the experiments on Re(VII) extraction we used the following organic reagents of the amine type: commercially pure tri-iso-octylamine (TIOA) of Hostarex A 324 brand (no less than 95% main substance and up to 5% primary and secondary amines), pure tri-n-octylamine obtained from "Vekton" (St.Petersburg, Russia) and commercially pure trialkylamine produced in Lermontov (Russia); and the reagents belonging to long-chain alcohols: 1-heptanol, 2-heptanol, 1-octanol, 2-octanol, 1- nonanol and 2-nonanol of "pure" grade, produced by "Viking" company (Voronezh, Russia) or by "Vekton" (St.Petersburg, Russia).

In the case of amine-type extraction, the extracting agents were the solutions containing 5-30% v/v of the amine in an Escaid 100 diluent with addition of 20% v/v isomeric aliphatic alcohols (1-octanol or 2-ethyl-hexanol-1 of "pure" grade). The extracting agent was preliminarily converted into the salt form via the contact with a H$_2$SO$_4$ solution of the same concentration as a solution of rhenium, from which the extraction was performed.

The extraction was performed in separatory funnels at a volume ratio of the organic to aqueous phase equal to 1:25 at room temperature in the course of 5 min, which provided attaining the equilibrium by the system.

The experiments on the temperature effect on the extraction were carried out in a constant-temperature round-bottomed flask with a volume of 0.25 ml supplied with a mechanical stirrer.

In the case of long-chain alcohols, the extracting agent was undiluted reagent. Since aliphatic alcohols are able to extract mineral acids [8], the extracting agents were preliminarily saturated with H$_2$SO$_4$ to prevent additional extraction of the mineral acid from concentrated acid media.

The extraction experiments were carried out at room temperature in 50-100 ml volumetric cylinders for 5 min at 1:1 organic to aqueous phase ratio.

Model rhenium-containing solutions were prepared by dissolution of pure-grade ammonium perrhenate in distilled water, with addition of a necessary amount of chemically pure sulfuric acid. The concentration of rhenium(VII) was about 0.001 mole/l (186.2 mg/l), and that of sulfuric acid, from 0.1 to 9 mole/l.

The content of rhenium(VII) in the aqueous phase was determined spectrophotometrically from the coloration intensity of the thiourea complex of rhenium(IV), formed in the presence of Sn(II) as reducing agent. The light absorption was measured with a KFK-3 photoelectric colorimeter at a wavelength $\lambda=390$ nm [9] or by the atomic-emission method on a "Plazma 400" spectrometer. The content of rhenium in the organic phase was calculated as the difference of its contents in the aqueous phase before and after extraction.

The sulfuric acid concentration in the aqueous phase was determined by titration.

Result and discussion

The obtained data are presented in Figures 1 and 2. It follows from Fig. 1 that irrespectively of the amine type, its concentration and process temperature, increasing of the acid concentration in the aqueous phase only causes the rhenium distribution to diminish (Fig.1), which is due to the anion-exchange mechanism of ReO_4^- extraction with amines:

$$(R_3NH)_2SO_4 + 2ReO_4^- \leftrightarrow 2R_3NHReO_4 + SO_4^{2-}.$$
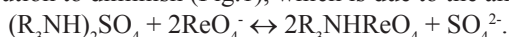
Apparently, any attempt to increase the sulphuric acid concentration will only decrease the rhenium concentration.

Both in weakly acidic (up to 2-3 mole/l H_2SO_4) and strongly acidic (>7.5 mole/l H_2SO_4) areas, the decline of rhenium distribution coefficients is more pronounced, which is due to changing forms of the extracting agent and the metal under these conditions. Thus, it is known that increasing the acidity to 2-3 mole/l H_2SO_4 converts practically the entire of $(R_3NH)_2SO_4$ into the organic phase to a bisulphate form – $[(R_3NH)HSO_4]_4$ [10], whereas at high H_2SO_4 concentrations a complex rhenium anion $[ReO_2(SO_4)_2]^-$ is formed [11], which undoubtedly tells on the extractional characteristics of the system.

Interestingly, we have failed to detect the numerously reported maxima on the $C(H_2SO_4)$-$D(Re)$ curve of rhenium extraction with amines. Apparently, the low $D(Re)$ values were obtained in a weakly acidic region due to analytical errors of spectrophotometric analysis [1-3, 6, 7]. We have noted that during the analysis of weakly-acidic samples by the spectrophotometric method [9] there appears a hardly noticeable colloid suspension (probably, SnO_2), which gives a higher value of the sample optic density, thus increasing the rhenium content in raffinates analyzed resulting in incorrect data. By applying atom-emission spectroscopy with inductive-bonded plasma (AAS ICP) to the weakly acidic raffinates, we eliminated this error and obtained reliable data on the acidity effect on rhenium extraction by tertiary amines.
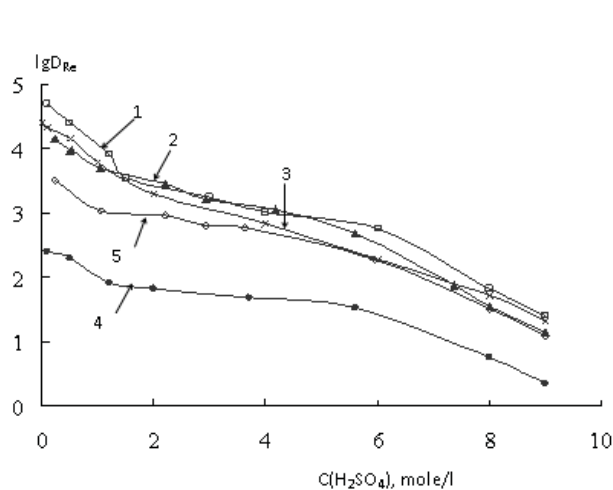

Fig. 1. The effect of H_2SO_4 concentration in the aqueous phase on lgD_{Re} during the rhenium (VII) extraction by tertiary amines, v/v: 30% ТиОА (1), 30% ТОА (2), 30% ТАА (3), 5% ТиОА at t=20°C (4), 30% ТиОА at t=55°C (5). O:W = 1:25, τ=5 min., C(Re) init. ~10^{-3} mole/l (0,2 g/l).
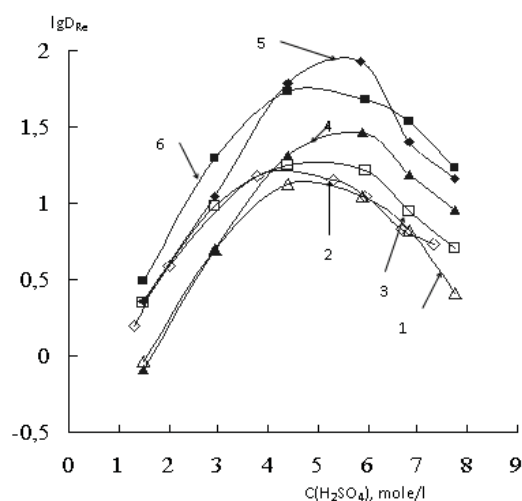
Fig. 2. The effect of H_2SO_4 concentration in the aqueous phase on D_{Re} during rhenium (VII) extraction by isomeric aliphatic alcohols C_7-C_9: 1-nonanol (1), 1-octanol (2), 1-heptanol (3), 2-nonanol (4), 2-octanol (5), 2-heptanol (6). O:W = 1:1, τ=5 min., C(Re) init. ~10^{-3} mole/l (0,2 g/l), t=20°C.

High-molecular aliphatic alcohols are predominantly used in rhenium technology as modifying additives in amine-containing extractive compositions. However, recent attention has been focused on the extractive properties of the alcohols proper [10].

Aliphatic alcohols, containing 7-9 carbon atoms in the chain, meet the principal requirements to industrial extracting agents being able to extract rhenium from acidic solutions, although not as efficiently as tertiary-amine

based agents. Since the extraction process with alcohols proceeds by the hydrate-solvate mechanism, according to the pattern:

$$ReO_4^- + H_3O^+ + nH_2O + qROH \leftrightarrow [H_3O(H_2O)_n (ROH)_q]^+ ReO_4^-,$$
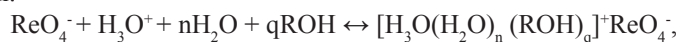
an increase in the metal extraction to the organic phase is observed at $C(H_2SO_4) \geq 1$-2 mole/l. As can be seen from Figure 2, the curves of $C(H_2SO_4)$-lgD(Re) dependences for all alcohol isomers C_7-C_9 pass through a maximum at $C(H_2SO_4)$ from 4 to 7 mole/l depending on their structure. On the one hand, this behavior of the curves is caused by increasing rhenium(VII) extraction by alcohols as acidity in the area of low and medium acid concentrations grows due to a shift in equilibrium towards the formation of a hydrate-solvate complex. On the other hand, this occurs due to inhibition of the rhenium(VII) extraction in the strongly acidic region as the competing process of H_2SO_4 extraction enhances.

Conclusion

Thus, it has been established that the effect of the sulphuric acid concentration on rhenium solvent extraction is largely due to the extraction process mechanism. In the case of the anion-exchange mechanism, ReO_4^- is best extracted from weakly acidic solutions, whereas when the hydrate-solvate mechanism is used – from solutions containing 4-7 mole/l H_2SO_4.

Acknowledgements

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