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Extraction of perrhenate anion from aqueous sulphuric acid medium and its thermodynamics

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ABSTRACT

Aqueous solution was simulated by ammonium perrhenate and sodium sulfate in sulphuric acid system according to waste water from metallurgy process of copper and molybdenum. Molalities of perrhenate after extraction were measured at ionic strength from 0.2 to 2.0 mol kg^{-1} at temperature range 278.15 K to 303.15 K, using tri-*n*-octylamine as extractant. Optimization condition of extraction was determined in this sulphuric acid medium. The standard extraction constants K^0 at various temperatures were obtained by method of polynomial approximation. Thermodynamic quantities for the extraction process were calculated.

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1. Introduction

Rhenium is one kind of scattered metals without solo mine. In copper and molybdenum mineral exploitation and metallurgy, the rhenium(VII) was separated as ash and immerged into the acid waste aqueous solution. The residual perrhenate in aqueous solution could result in heavy metal pollution, more badly, the Re 187 has radioactivity, which could cause grisliness radiant damage [1–5].

In industry, the waste water from metallurgy was purified by some sewage disposal process, but their emphasis is heavy metals removals which are almost cation status. The perrhenate will still kept in concentrates with moderate concentration. So the removal of perrhenate ion from wastewater and residual becomes of great significant [6].

Solvent extraction method is used especially for separation of rhenium from other components, such as arsenic, tungsten ormolybdenum. Most frequently, for rhenium extraction, tri-*n*-octylamine, bis-isododecylamine, pyridine, Aliquat336, tributyl phosphate, trioctylphosphine oxide, cyklohexanon, ethyl xanthate and mesityloxide were used [7,8]. In the process of rhenium stripping from organic phase, solutions of both acids and alkalis were used, i.e., aqueous HCl, H_2SO_4 and ammonium solution (for ammonium perrhenate separation) or aqueous solutions of NaOH and KOH [9].

The hydrometallurgy of copper and molybdenum are usually in sulphuric acid medium. So the separation of perrhenate from these systems became the focus of recent research [10–13]. The common amine extractant, tri-*n*-octylamine, provides high extent of extraction of metal anions [14,15]. Also it is an effective extractant for perrhenate, which has stable molecular structure. The purpose of this study is to investigate the recovery of rhenium(VII) from sulphuric acid medium which simulated waste aqueous solution from metallurgy, and the physicochemical properties in the extraction process.

2. Experimental

The residual concentrates of industry was simulated with sulphuric acid, ammonium perrhenate, and sodium sulfate as impurities remained in residual.

The water used was doubly deionized with a conductivity of $1.5 \times 10^{-4}\ \Omega^{-1}\ m^{-1}$. The Na_2SO_4, was of AR (analytical reagent) grade (99.5% mass pure) from Shanghai reagent Co., Ltd., H_2SO_4, *n*-C_7H_{16} and tri-*n*-octylamine were of AR (analytical reagent) grade (99% mass pure) from Shanghai reagent Co., Ltd. NH_4ReO_4 was (99% mass pure) from Jiangxi Copper Co., Ltd. The *n*-C_7H_{16} used as diluent was of AR grade with density as $\rho = 0.68 \times 10^3$ kg/m^3. The source and purity of the materials are listed in Table 1.

The aqueous phase was prepared by dissolving NH_4ReO_4 in an aqueous solution of H_2SO_4 of constant molality. The initial molality of the NH_4ReO_4 was $a = 0.001$ mol kg^{-1}, and the initial molality of the H_2SO_4 was $c = 0.1$ mol kg^{-1}. The Na_2SO_4 was used to adjust the

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Table 1
The sources and purity of the materials.

Mass fraction purity	Source
Sulphuric acid ≥0.99 (L)	Shanghai Reagent Co., Ltd.
Ammonium perrhenate ≥0.99	Jiangxi Copper Co., Ltd.
Sodium sulfate ≥0.99	Shenyang Reagent Co., Ltd.
N-heptane ≥0.99 (L)	Shenyang Reagent Co., Ltd.
tri-*N*-octylamine ≥0.99 (L)	Shanghai Organic Chemistry Institute

L: is for liquid, others are solid.

impurity concentration I (ionic strength) of the aqueous solution to 0.1–2.0 mol kg^{-1}. The organic phase was prepared by dissolving tri-*n*-octylamine in n-C_7H_{16}, the initial molality of tri-*n*-octylamine being kept constant ($b = 0.02$ mol kg^{-1}).

A volume (10 cm^3) of the organic phase was brought into contact with the same volume of aqueous phase in an extraction bottle and the two-phase mixture was shaken mechanically for 15 min. The extraction bottles were kept at different temperatures: 278.15, 283.15, 288.15, 293.15, 298.15 and 303.15 K, within ±0.05 K. After standing for 15 min, the two phases were separated and the molality of ReO_4^- ($m\{ReO_4^-\}$) in the equilibrium aqueous phase was determined using a 722 spectrophotometer with uncertainty ±0.01 for three replicate measurements. The results are shown in Table 2 and Fig. 1.

3. Results and discussion

3.1. Optimization condition of extraction

It is shown from Table 2, the acidity of the extraction system decreased with the increasing of ionic strength, which indicated the more impurity, the more acid needed. The remained ReO_4^- increased with the increasing to temperature, which revealed the extraction was inclined to low temperature. The corresponding data were also shown in Fig. 1 as below.

The extractant has satisfactory extraction effect at various temperatures of the experiment. The extraction efficiency is almost above 99%, which indicated the extraction progress performed completely. Furthermore, molalities of remained ReO_4^- in aqueous phase are little at low temperature and low ionic strength, which indicates the best extraction conditions. In industry, the system should be kept in high acidity and little impurities at low temperature.

Table 2
Extraction process data values of pH and ReO_4^- concentration in the componets of {H_2SO_4(a) + Na_2SO_4 (a) + NH_4ReO_4 (a) + H_2O (a) + tri-*n*-octylamine (o) + nC_7H_{16}(o) + $H{\cdot}NR_3{\cdot}ReO_4$ (o)} at temperatures from 278.15 to 303.15 K.

T (K)	278.15	283.15	288.15	293.15	298.15	303.15
			$I = 0.2$			
pH	1.38	1.46	1.46	1.56	1.36	1.20
m ReO_4^- (10^{-6})	0.527	1.48	3.23	4.39	6.95	19.2
			$I = 0.4$			
pH	1.37	1.43	1.54	1.65	1.43	1.21
m ReO_4^- (10^{-6})	0.275	1.75	3.48	4.48	12.5	26.0
			$I = 0.5$			
pH	1.48	1.45	1.55	1.64	1.62	1.25
m ReO_4^- (10^{-6})	0.621	1.8	3.73	5.13	13.2	32.5
			$I = 0.6$			
pH	1.46	1.48	1.61	1.69	1.76	1.38
m ReO_4^- (10^{-6})	0.931	2.42	4.01	5.52	16.1	36.3
			$I = 0.8$			
pH	1.48	1.53	1.66	1.75	1.75	1.43
m ReO_4^- (10^{-6})	0.931	1.99	4.23	6.51	16.8	42.8
			$I = 1.0$			
pH	1.35	1.67	1.68	1.73	1.65	1.51
m ReO_4^- (10^{-6})	0.497	3.73	4.47	6.77	21.5	49.9
			$I = 1.2$			
pH	1.5	1.59	1.69	1.75	1.76	1.46
m ReO_4^- (10^{-6})	0.993	2.05	5.46	8.13	25.9	55.4
			$I = 1.4$			
pH	1.55	1.62	1.71	1.8	1.98	1.58
m ReO_4^- (10^{-6})	1.13	2.79	7.08	10.5	30.2	55.9
			$I = 1.5$			
pH	1.72	1.72	1.74	1.81	1.75	1.54
m ReO_4^- (10^{-6})	1.34	4.53	7.45	11.8	25.9	62.1
			$I = 1.6$			
pH	1.45	1.64	1.77	1.83	1.83	1.63
m ReO_4^- (10^{-6})	1.50	3.66	7.82	11.9	35.5	70.2
			$I' = 1.8$			
pH	1.66	1.67	1.81	1.89	1.92	1.74
m ReO_4^- (10^{-6})	1.53	3.79	6.89	13.6	38.1	71.0
			$I = 2.0$			
pH	1.55	1.69	1.75	1.90	1.95	1.82
m ReO_4^- (10^{-6})	1.56	5.22	8.20	14.9	44.1	73.7

m is the molar concentration (mol kg^{-1}), T is Kelvin temperature, I is ionic strength (molar concentration, (mol kg^{-1}). Standard uncertainties u are $u(T) = \pm 0.05$ K, $u(p) = \pm 10$ kPa, and the combined expanded uncertainty Uc is $Uc(\rho) = \pm 5 \times 10^{-7}$ mol kg^{-1} (0.95 level of confidence).

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