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Selective extraction of nitric and acetic acids from etching waste acid using N235 and MIBK mixtures

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ABSTRACT

The selective extraction of nitric and acetic acids from a simulated etching waste acid was investigated using a mixture of the extractants Alamine 336 (N235) and methyl isobutyl ketone (MIBK). The effects of dilution of the etching waste acid, N235 and MIBK concentrations, organic/aqueous (O/A) phase ratio, extraction temperature, and contact time were systematically studied. The results demonstrate that with an extractant mixture of the composition 12.5 vol% N235 and 87.5 vol% MIBK, 75% acetic acid and 85% nitric acid were extracted. However, only 3% phosphoric acid was co-extracted in a single-stage contact under the following conditions: phosphoric acid concentration of 385 g/L in the diluted acid, O/A ratio of 1.5:1, reaction temperature of 25–35 °C and reaction time of 10 min. The McCabe-Thiele analysis predicts that over 98% acetic acid and 99% nitric acid can be extracted, with co-extraction of only 5% phosphoric acid through a three-stage counter-current operation at an O/A ratio of 3:2. Further, ~99% HNO_3, 99% HAC, and 99% H_3PO_4 loaded in the organic phase were stripped using 0.25 mol/L $NH_3 \cdot H_2O$ as the stripping agent at an O/A ratio of 1:2. Therefore, it is feasible to achieve almost complete separation of nitric acid and acetic acid from the waste acid to obtain purified phosphoric acid and a binary compound fertilizer containing the nutritional elements nitrogen and phosphorus. The compositions of the extraction complexes of different acids were determined to be $H_3PO_4 \cdot 2N235$, $HAC \cdot 1.5N235$ and $HNO_3 \cdot N235$ for the N235 extraction and $HAC \cdot 2MIBK$ for the MIBK extraction of HAC. The results can explain the extraction tendencies of the three acids obtained above. Analyses of the FT-IR spectra of the loaded organic phases indicate that the N235 extraction of HNO_3 occurred by the ion pair association mechanism, while the acetic acid extraction using N235 or MIBK was realized through hydrogen bonding.

1. Introduction

The semiconductor etching process discharges large quantities of waste acids containing approximately 50–70 wt% (680–1100 g/L) phosphoric acid, 2–10 wt% (100–200 g/L) acetic acid, 1–10 wt% (30–100 g/L) nitric acid and 10–20 wt% (80–200 g/L) hydrofluoric acid, in addition to metal impurities such as aluminum and molybdenum. Globally, more than one billion cubic meters of waste etchants are generated annually with an annual increase of 15–18% [1]. Until recently, these waste acids have been generally treated with a combined chemical and biochemical process, in which the acids are first subjected to lime neutralization to separate the phosphoric acid component in the form of calcium hydrophosphate, and the acetate and nitrate ions remaining in the neutralized mother solution are further removed in the activated sludge process. This process not only wastes resources but also has a high cost [2]. Complete neutralization of the waste acids using ammonia has also been reported [3], which has poor economy due to low production of the added-value binary compound fertilizer.

The recovery of valuable inorganic and/or organic acids from waste acids has attracted wide attention, and these studies generally use traditional distillation for this purpose [4–10]. With the combination of diffusion dialysis and vacuum distillation, Kim et al. [8] achieved complete separation of HNO_3 and HAC from H_3PO_4 at 730 mmHg vacuum pressure and 125 °C. However, the H_3PO_4 recovery yield was less than 80%. Yamamoto et al. [9] studied the separation of hydrofluoric acid and nitric acid by distillation of etching solutions, based on the different salt effects of $CsNO_3$ on the HF-H_2O and HNO_3-H_2O systems. Ni et al. [10] used a combined partial neutralization pretreatment (PNP) and distillation strategy to recover acetic acid from a HAC-HNO_3-H_3PO_4 waste acid mixture in a facile manner. In their study, 94.3% HAC with a purity of 99.4 wt% could be efficiently recovered by using NaOH as the neutralizer at a distillation temperature of 140 °C.

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Solvent extraction is another competitive route to recover inorganic and/or organic acids from etching waste acids due to its high selectivity and energy efficiency. Two types of extractants have been widely investigated, i.e., neutral extractants and tertiary amine extractants [11–20]. Among the neutral extractants, Shin et al. [11,14] recovered over 95% acetic and nitric acids, respectively, from HAC-HNO_3-HF waste acids by using 2-ethylhexyl alcohol (EHA) and tributyl phosphate (TBP) as extractants. Yoshinori Motoda et al. [12] proposed a process for the recovery of phosphoric acid from HAC-HNO_3-H_3PO_4 waste acids, in which approximately 97% of nitric acid and 95% of acetic acid were extracted by tri-octyl phosphate (TOP) through a 6-stage countercurrent operation. Mitchell et al. [17] selected TBP as the most promising solvent for the extraction of acetic acid from HAC-HNO_3-H_2O mixed waste acids. Among the tertiary amine extractants, Jia et al. [18] discovered that tri-n-octylamine (TOA) is an effective extractant to separate nitric acid from the HNO_3/H_3PO_4/H_2O system. With 0.25 mol/kg TOA as extractant, significant amounts of acetic acid could be removed from a mixture of succinic and acetic acids after a three-stage successive extraction [19].

A survey of the literature indicates that although many extractants can extract acetic acid and/or nitric acid from H_3PO_4-HAC-HNO_3 mixed waste acids, highly efficient, simultaneous separation of nitric and acetic acids to obtain purified phosphoric acid has seldom been reported. In this work, the extractive recovery of phosphoric acid from a simulated HAC-HNO_3-H_3PO_4 etching waste acid was investigated, using an extractant mixture consisting of MIBK and N235. The effects of process parameters on the selective separation of acetic and nitric acids over phosphoric acid, the extraction complex composition, and extraction mechanism were investigated.

2. Experimental

2.1. Reagents and solutions

The simulated etching waste acid (abbreviated as SEWA hereafter) employed in the study was prepared using analytical grade acetic, nitric and phosphoric acids provided by Chengdu Kelong Chemical Reagent Factory. The preparation was carried out according to the chemical compositions and the average concentrations of the etching waste acids discharged during the manufacturing process of liquid crystal displays (LCD) in Foxconn Company, Chengdu. The concentration of each acid is presented in Table 1. Generally, the LCD etching spent acids also contain small amounts of aluminum and molybdenum ions, usually at an order of magnitude of ~100 mg/L. Because the main objective of this research is to separate the three acids and feasible methods for separation of phosphoric acid from various metal ions have been well established in the wet process for phosphoric acid purification [21,22], the SEWA were prepared without addition of aluminum and molybdenum ions. MIBK (99%) was provided by Chengdu Kelong Chemical Reagent Factory. Alamine 336 (R_3N, $R = C_{8-10}$) (98%) and TBP (99%) were obtained from the Shanghai Laiyashi Chemical Reagent Factory. Technical grade kerosene was used as a diluent in the extractant screening experiment while cyclohexane (99.5%) was employed as a diluent in the study of the extraction complex composition and extraction mechanism. All of the reagents were used as received without any further purification.

Table 1
Chemical composition of the simulated etching waste acid (SEWA).

Component	H_3PO_4	HNO_3	HAC
Concentration (g/L)	770	50	147

2.2. Procedures

All extraction experiments were carried out in a 250-mL three-necked glass flask. A mechanical stirrer was used to mix the two liquid phases. The reactor was heated using a water bath, which controlled the temperature to within ±2 °C. In each test for the process optimization experiments, certain volumes of the SEWA or diluted SEWA and organic phase (N235+ kerosene, MIBK+ kerosene, TBP+ kerosene, or N235+ MIBK), which had been preheated separately to the required temperatures, were added to the reactor. The two phases were mixed at a constant stirring rate of 200 rpm. After a set period of time, the stirring was stopped. In the investigations of extraction complex composition and extraction mechanism, the diluted SEWA and N235+ cyclohexane or MIBK+ cyclohexane were added to the reactor and brought into contact at 30 °C. The resulting solutions were then transferred to a separating funnel and allowed to settle for 10 min. After phase disengagement, the acetic, nitric and phosphoric acid concentrations in the raffinate were measured, which allowed the calculation of the distribution coefficient, extraction efficiency and separation factor. The loaded organic phase was characterized by FTIR.

All stripping experiments were carried out in a 250-mL three-necked glass flask. For each test, equal volumes of the loaded organic phase and aqueous ammonia were brought into contact at 25 °C and 200 rpm for the required time. The resulting solutions were then transferred to a separating funnel and allowed to settle for 10 min. After phase disengagement, the nitrate and phosphate ion concentrations in the strip liquor were determined, the acetic acid concentration in the organic phase was measured by GC-MS, and the stripping efficiency of each acid was calculated.

Parallel experiments were conducted to check the accuracy of the extraction and stripping experiments. The results show that the absolute error was within ±2%.

The distribution coefficient D was calculated according to Eq. (1):

$$D = \frac{[\mathrm{HA}]_{org}}{[\mathrm{HA}]_{aq}} \tag{1}$$

where $[\mathrm{HA}]_{org}$ and $[\mathrm{HA}]_{aq}$ represent the equilibrium concentrations of each acid in the organic and aqueous phases, respectively. From the D value, the extraction efficiency (E) of each acid was calculated by Eq. (2). The separation factors between HAC and H_3PO_4 (β_1) and between HNO_3 and H_3PO_4 (β_2) were calculated according to Eqs. (3) and (4), respectively. The stripping efficiency (SE) of each acid was estimated using Eq. (5).

$$E = \frac{D}{D + \frac{V_{aq}}{V_{org}}} \tag{2}$$

$$\beta_1 = \frac{D_{HAC}}{D_{H_3PO_4}} \tag{3}$$

$$\beta_2 = \frac{D_{HNO_3}}{D_{H_3PO_4}} \tag{4}$$

$$\mathrm{SE} = 1 - \mathrm{E} \tag{5}$$

where V_{aq} and V_{org} are the volumes of aqueous and organic phases, respectively.

2.3. Analysis and characterization

The total amount of acid in the raffinate was measured by acid-base titration. The phosphoric and nitric acid concentrations were determined, respectively, by quinoline molybdate gravimetric and redox titration methods. The acetic acid concentration was derived