



# Extraction of hydrochloric acid with binary mixtures of tertiary amine and organophosphorus acid and analysis of the interaction between the constituents of these mixtures



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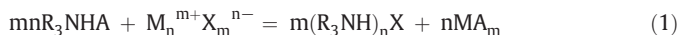
## ABSTRACT

Binary mixtures of tertiary amine and acidic extractant showed synergism on the extraction of metals from a weak acid solution but there is uncertainty in identifying the solvent extraction reaction. The nature of interaction between the extractants in the binary mixture affects synergism in extraction reaction. In order to correlate the interaction with the physical properties of each extractant in the binary mixture, extraction of HCl from dilute solution in the absence/presence of rare earth elements (REEs) has been investigated. The extraction order of HCl and REEs was: Cyanex 272 + Alamine 336 > PC88A + Alamine 336 > D2EHPA > Alamine 336. The interaction between strong acidic extractant (D2EHPA) and Alamine 336 was strong enough to form an amine salt which took part in the reaction. In the binary mixture of weak acidic extractant (Cyanex 272 and PC88A) and Alamine 336, each extractant took part in the reaction independently.

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## 1. Introduction

The binary mixtures consisting of amines and acidic extractants have been widely used for the extraction of various metals, such as alkali and alkaline earth chlorides (Davis and Grinstead, 1970; Grinstead et al., 1969; Grinstead and Davis, 1970; Hanson et al., 1975), PGMs (Belova et al., 1988) and some of transition metals (Kress et al., 1989; Sato et al., 1980), etc. In most cases, an amine salt ( $R_3NHA$ ) is formed and this amine salt extracts neutral metal salts similar to solvating extraction mechanism, which is represented as



where  $R_3N$  and  $HA$  are tertiary amines and acidic extractants, respectively, and  $M_n^{m+}X_m^{n-}$  is the metal salts. According to Eq. (1), no protons are involved in the reaction. Therefore, there should be little difference in the solution pH before and after the extraction. In the extraction of rare earths from chloride solutions by the binary mixtures of D2EHPA and tertiary amine, the solution pH was little changed during the extraction (initial pH = 5.2; equilibrium pH = 5.0) (Kalyakin et al., 2011, 2015). In the synergistic solvent extraction of Pr and Nd by the binary mixtures of Cyanex 272 and tertiary amines from chloride solutions, however, the equilibrium pH was lower than initial pH but higher than that by single Cyanex 272 (Liu et al., 2014). A similar behavior

has been reported in the extraction of  $ZnCl_2$  and  $ZnSO_4$  by the binary mixtures of D2EHPA/lauric acid and amine extractants (Eyal et al., 1994a,b). The variation in the pH values indicated that the rare earth metals were extracted by Cyanex 272, while the synergism was ascribed to the extraction of hydrogen ions by tertiary amines. Therefore, the interaction between tertiary amine and organophosphorus acid extractant in the binary mixtures might affect the extraction mechanism.

Mixtures of amine and acidic extractant have also been found to be efficient on the extraction of strong acids (Baniel, 1981; Eyal and Baniel, 1982; Eyal, 1996). Additionally, these mixtures have a positive effect on the stripping of acid from the loaded organic compared to single amines (Belova et al., 2007; Eyal et al., 1986; Tait, 1993). The extraction of HCl (Eyal et al., 1990),  $H_2SO_4$  (Eyal et al., 1990), and  $H_3PO_4$  (Baniel et al., 1989) by different mixtures of amine and acidic extractant has been widely studied. In the extraction of inorganic acid by the mixtures of amine and acidic extractant, the nature of each extractant in the mixture and the interaction between them significantly affected the extraction of inorganic acid.

According to the literature on the extraction of metals with the binary mixture of tertiary amine and acidic extractant, either an amine salt or a free acidic extractant is responsible for the extraction. The basic question is to correlate the extraction reaction with the physical properties of the extractants in the extraction of metals with these binary mixtures. For this purpose, experiments have been done on the solvent extraction of hydrochloric acid with the binary mixtures of tertiary amine and organophosphorus acid extractant in the absence and presence of rare earth metals (La, Ce, Pr and Nd). The effect of basicity of

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amines, acidity of organophosphorus acid extractant and the composition of the mixtures on the extraction of hydrochloric acid and rare earth metals has been studied. Based on the difference in equilibrium pH obtained after extraction by different binary mixtures, the difference in extraction mechanism is discussed.

## 2. Experimental

### 2.1. Reagents and chemicals

Cyanex 272, D2EHPA and PC88A were purchased from Cytec Industries, Canada. Alamine 336 and TEHA (tri-2-ethylhexyl amine) were received from BASF Co., and TOA (tri-n-octylamine) was purchased from Samchun Pure Chem Co., Ltd, respectively. All the extractants were used as received without any further purification. Kerosene (Daejung Co.) was employed as a diluent for the present work except for the study on the effect of diluents.

Lanthanum, cerium, praseodymium and neodymium chlorides (99.9%) were purchased from Alfa Aesar (A Johnson Matthey Company). The synthetic solutions were prepared by dissolving the corresponding chloride salts. Concentrated HCl and NaOH solutions were used to adjust the initial pH of the aqueous solutions. All other reagents used were of analytical grade.

### 2.2. Solvent extraction procedure

The extraction was carried out by shaking equal volume of aqueous and organic phases in a screwed cap bottle for 20 min with a wrist action shaker (Burrell, USA). The initial and equilibrium pHs of the solution were measured by a pH meter (Orion Star A221 model). In calculating the extraction percentage of hydrogen ion, the concentration of hydrogen ion was obtained from the solution pH by assuming that the concentration of hydrogen ion was equal to the activity of hydrogen ion. Metal concentration in the aqueous phase before and after extraction was determined by ICP-AES (OPTIMA 8300, Perkin Elmer). Metal concentration in the organic phase was obtained by mass balance.

## 3. Results and discussion

### 3.1. Extraction of hydrochloric acid by single Alamine 336

In solvent extraction of metals with tertiary amines, tertiary amines should be protonated by an acid to act as an anion exchanger. Generally, protonation reaction of tertiary amine ( $R_3N$ ) can be considered to occur in the aqueous phase. The protonated amine combines with the anion radical of the acid and then this combined molecule is transferred to the organic phase. The protonation reaction of tertiary amine can be represented as follows



$$K_{R_3N, \text{protonation}} = \frac{[R_3NH^+]_{org}}{[R_3N]_{org} [H^+]_{aq}}$$

where  $K_{R_3N, \text{protonation}}$  is the protonation constant of a tertiary amine. From Eq. (2), the following equation is obtained

$$\log \left( \frac{[R_3NH^+]_{org}}{[R_3N]_{org}} \right) = \log K_{R_3N, P} - pH \quad (3)$$

For a given tertiary amine, Eq. (3) indicates that the concentration ratio of the protonated amine to free amine depends on the magnitude of protonation constant of a tertiary amine as well as solution pH. In order to investigate the extraction behavior of hydrogen ion by Alamine 336, the initial pH of HCl solutions was varied from 0.95 to 4.98. Table 1 shows the variation in the equilibrium pH of these HCl solutions after

**Table 1**

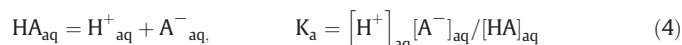
Change in the values of pH before and after the extraction by single 0.5 M Alamine 336.

| Initial pH     | 0.95 | 1.90 | 3.00 | 4.00 | 4.98 |
|----------------|------|------|------|------|------|
| Equilibrium pH | 1.17 | 2.65 | 4.58 | 4.66 | 4.98 |

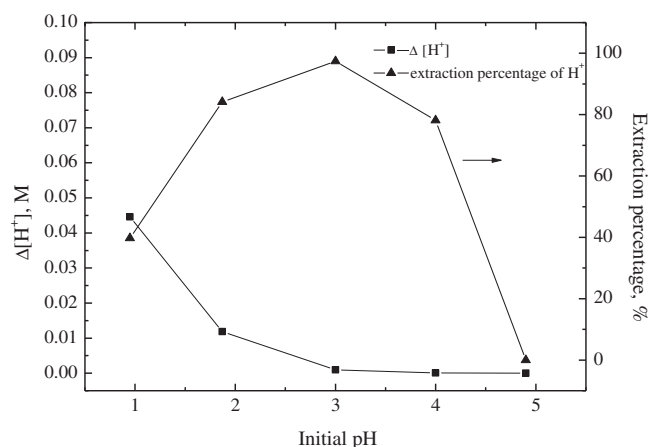
the extraction with 0.5 M Alamine 336. Except when the initial pH of the solution was 4.98, the equilibrium pH increased. Fig. 1 shows the extraction percentage of hydrogen ion together with the change in the concentration of the hydrogen ion extracted by Alamine 336. As the initial pH increased from 0.95 to 3, the extraction percentage of hydrogen ion increased and further increase of initial pH from 3 to 4.98 resulted in a decrease in the extraction percentage of hydrogen ion. This extraction behavior of hydrogen ion with initial pH can be explained by using Eq. (3). The protonation constant of Alamine 336 is about  $3.16 \times 10^{-3}$  ( $\log K_{R_3N, P} = 3.5$ ) (Eyal and Canari, 1995). Therefore, the concentration ratio of the protonated amine to free amine begins to decrease when the equilibrium pH is higher than 3.5. This agrees well with our results in the solution pH range of 3 to 4.98. When the equilibrium pH was lower than 3, however, the extraction percentage decreased with decrease of solution pH. Although the extraction percentage of hydrogen ion became lower as the solution pH decreased from 3 to 1, the change in the concentration of hydrogen ion owing to the extraction by Alamine 336 increased rapidly in these conditions.

### 3.2. Extraction of hydrochloric acid by binary mixtures of amine and organophosphorus acid extractant

In the extraction of metal ions by organophosphorus acid extractants, some of the extractant first dissolve in the aqueous phase and then dissociate into hydrogen and the anion group of the extractant. The dissociation of the organophosphorus acid extractants in aqueous phase is represented as



where  $K_a$  represents the dissociation constant of organophosphorus acid extractant. Dissociation degree of an organophosphorus extractant depends on its dissociation constant ( $K_a$ ). The dissociation degree of some organophosphorus acid extractants (D2EHPA, PC88A, Cyanex 272) was compared by contacting this extractant with HCl solution at several concentrations. In these experiments, the concentration of each extractant was kept at 0.5 M. From Table 2, it is clear that the decrease in equilibrium pH was more prominent as the initial pH increased. The decrease in equilibrium pH of the solution after contact followed the order: D2EHPA > PC88A > Cyanex 272. Based on the



**Fig. 1.** Effect of solution pH on the extraction of hydrogen by single 0.5 M Alamine 336.

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