



# Effect of the diluents on the interaction between components in the binary mixtures of organophosphorus acid and tertiary amine



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## ABSTRACT

In the extraction of rare earth elements (REEs) from chloride solutions by binary mixtures of organophosphorus acid and tertiary amine, the acid-base equilibria in the mixtures and the nature of the diluents affected the synergistic effect. In order to correlate the interaction in the mixtures with the dielectric constant of the diluents, the FT-IR spectra together with the viscosities of individual extractants and binary mixtures in three diluents (*n*-hexane, xylene, and toluene) were analyzed. The excess viscosities of the mixtures in different diluents were obtained as a function of composition. The IR spectra and excess viscosity data indicated that the interaction between acidic and amine extractants in the binary mixture grew stronger as the dielectric constant of a diluent became lower.

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## 1. Introduction

Various solvent extraction systems like acidic, basic, neutral extractants and their mixtures have been widely employed in the separation and purification of rare earth elements (REEs) [1–7]. In these systems, the extractants are dissolved in a diluent which normally comprises the major portion of a system [8]. The reasons for using a diluent in the solvent extraction systems are to decrease the viscosity of the extractant, to provide a suitable concentration of extractant, and to decrease emulsion-forming tendencies of the extractant. It has been found that in many solvent extraction systems the diluents are not inert but have a marked effect on the metal extraction characteristics [9–11]. Among the several physical properties of diluents, the polarity of the diluents has a significant effect on the extraction of the REEs by various single extractants and mixtures [12–15]. The polarity of a diluent is proportional to its dielectric constant and lower dielectric constant means lower polarity [16]. The values of relative polarity and the dielectric constant of several diluents are listed in Table 1.

In the extraction of Pr and Sm by Cyanex 923 from nitrate solution, the diluent with a lower dielectric constant shows a higher extraction percentage [9]. In the synergistic solvent extraction of REEs from a chloride-acetate solution by the mixture of 8-Hydroxyquinoline and PC88A (2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester) [17, 18], and by the mixture of thenoyltrifluoroacetone (HTTA) and the quaternary ammonium salt (Aliquat 336) [19], the same trend was observed, namely the extraction percentage increased with decreasing

dielectric constant of the diluent. The higher extraction percentage of a metal by extractants in a diluent with smaller dielectric constant may indicate that the interaction between the diluent and an extractant is inversely proportional to the dielectric constant of the diluent [8,19,20]. However, the reverse trend is observed in the synergistic extraction of Pr and Nd by using binary mixtures of 0.5 M Cyanex 272 (bis(2,4,4-trimethylpentyl) phosphinic acid) and 0.5 M Alamine 336 (trioctyl/decyl amine) [21–22]. In these experiments, the extraction percentage of Pr and Nd is proportional to the dielectric constant of the diluents as follows: hexane < kerosene < xylene < toluene < benzene < chloroform. Similar extraction sequence is also found in the extraction of Nd by a mixture of Cyanex 302 and Alamine 308 (Triisooctylamine) [3].

In the synergistic extraction of Pr and Nd from chloride solutions with the above-mentioned binary mixtures, the synergistic effect depends on the interaction between the components in the mixtures [23]. As the interaction between the extractants in the mixture becomes weaker, the synergistic enhancement factor increases. The FT-IR spectra results of the mixtures confirmed that the strength of the interaction between the extractants in the mixture increases with the increase in the acidity of acidic extractant and the basicity of the amine extractant [24]. Since the properties of the diluent can influence the interaction between extractant and diluent, they might also affect the interaction between acidic and amine extractants in the binary mixture and thus the extraction of REEs. Furthermore, the excess properties, such as density, viscosity, and dielectric constant, can indicate the strength of the interaction in liquid mixtures [25–27]. Among the above-mentioned properties of liquid solutions, viscosity of liquid mixtures has been studied to determine the interaction in the mixtures [28–30]. In this work, the FT-IR and excess viscosity data of single and binary mixtures in 3 diluents (*n*-hexane, xylene and toluene) was compared to detect any

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**Table 1**  
Dielectric constants of commonly used diluents in solvent extraction.

Diluent	Relative polarity <sup>a</sup>	Dielectric constant
Kerosene	/	1.8
<i>n</i> -hexane	0.009	1.88
Octane	/	1.95
Cyclohexane	0.006	2.02
Carbon tetrachloride	0.052	2.24
Xylene	0.074	2.28
Benzene	0.111	2.30
Toluene	0.099	2.36
Chloroform	0.259	4.81

<sup>a</sup> The polarity value of water is consider as 1.000.

changes in the characteristic bands of each extractant and to get valuable information on the interactions occurring in these mixtures. Based on these data, the effect of the diluents on the interactions occurring in the organic phase, such as solute-solute and solute-solvent was discussed.

## 2. Experimental

### 2.1. Reagents and chemicals

Alamine 336 (tri-octyl/dodecyl amine, 95%), was purchased from BASF Co. The organophosphorus acid extractants used in the present study were D2EHPA (di-2-ethylhexyl phosphoric acid, Daihachi Chemicals, 95%), PC88A (Daihachi Chemicals, 95%), and Cyanex 272 (Cytec Inc., 85%). *N*-hexane (Duksan Pure Chemicals, EP), xylene (Daejung Chemicals & Metals, EP) and toluene (Duksan Pure Chemicals, EP) were employed as diluents. In previous studies on the synergistic extraction of REEs by binary mixtures and interaction between extractants in these mixtures, synergism was found by employing extractants as received without purification and the best composition for the synergistic extraction of REEs was found to be 0.5 M for both acidic and amine extractants. Therefore, in order not to affect the synergism or interaction, the reagents were also used without purification and the concentration of extractant was chosen at 0.5 M except the viscosity study. The mixtures were prepared by mixing tertiary amine, organophosphorus acid, and diluent in desired composition.

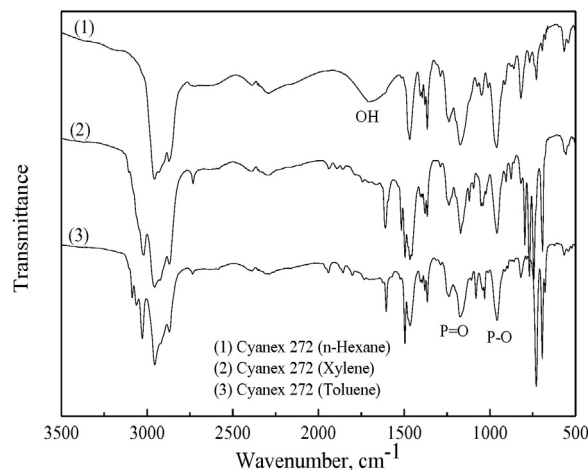
### 2.2. Apparatus and measurement

Fourier transform infrared spectroscopy (FT-IR) measurements of the binary mixtures in different diluents were performed with a Microscopic FT-IR/Raman Spectrometer (Vertex 80 V, Bruker, Germany) in a KBr demountable Cell. The infrared spectra of the organic solutions were taken in the range of 4000–550  $\text{cm}^{-1}$ . The viscosities of the binary mixtures in different diluents were measured using a Cannon-Fenske Routine Viscometer at 293 K.

## 3. Results

### 3.1. FT-IR spectra of single organophosphorus acid and tertiary amine extractants in different diluents

In order to elucidate the effect of diluent on the interaction between organophosphorus acid and tertiary amine in binary mixtures, infrared spectra measurements were done for individual extractant and binary mixtures in different diluents (*n*-hexane, xylene, and toluene). The IR spectra of individual organophosphorus acids (D2EHPA, PC88A, and Cyanex 272) and tertiary amine (Alamine 336) in different diluents are presented in Figs. 1–4. For comparison, all of the frequencies of characteristic bands of the extractants are shown in Table 2. In the FT-IR spectra of organophosphorus acids diluted in *n*-hexane (see (1) in Figs. 1–3), the characteristic stretching vibrational bands were shown



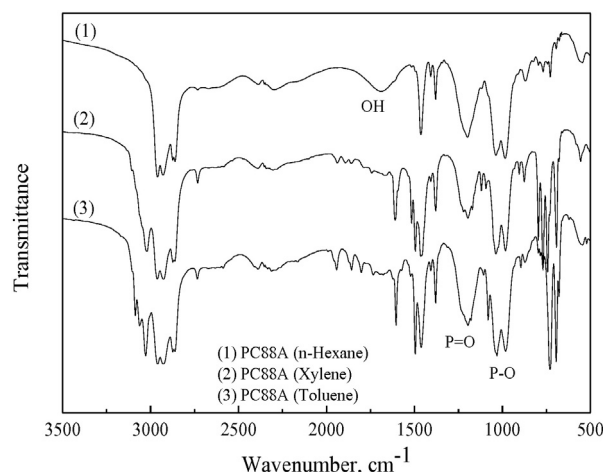
**Fig. 1.** IR spectra of 0.5 M Cyanex 272 in different diluents.

at 1172  $\text{cm}^{-1}$  (Cyanex 272), 1198  $\text{cm}^{-1}$  (PC88A) and 1230  $\text{cm}^{-1}$  (D2EHPA) for P=O, and 960  $\text{cm}^{-1}$  (Cyanex 272), 1036  $\text{cm}^{-1}$  (PC88A) and 1034  $\text{cm}^{-1}$  (D2EHPA) for P-O (P-O-C and P-O-H may be overlapped in the same frequency), respectively. The band at around 1706, 1693, and 1697  $\text{cm}^{-1}$  in the spectra of Cyanex 272, PC88A, and D2EHPA in *n*-hexane was due to the aggregative OH vibration between intermolecular H-bonding in the dimeric form. However, the OH vibration bands for the acidic extractants observed in *n*-hexane were no longer observed in xylene and toluene.

In the case of aliphatic amines, their characteristic bands (C-N stretching vibration) were observed as medium bands in the range of 1020–1250  $\text{cm}^{-1}$ . The peak (1096  $\text{cm}^{-1}$ ) appeared in the spectra of Alamine 336 in *n*-hexane. The C-H bending groups of xylene (1094 and 1039  $\text{cm}^{-1}$ ) and toluene (1080 and 1035  $\text{cm}^{-1}$ ) may be overlapped in the same range. Therefore, the C-N band of Alamine 336 in xylene and toluene was difficult to determine. The bands at around 1610  $\text{cm}^{-1}$  in all spectra are C-C stretches in the aromatic ring of xylene and toluene.

### 3.2. FT-IR spectra of binary mixtures of organophosphorus acid and tertiary amine extractants in different diluents

The interaction between components in a mixture affects the characteristic bands of IR spectra [31–33]. Therefore, the strength of the interaction in an extractant mixture can be determined by investigating the change of characteristic bands in the IR spectra of extractant. For



**Fig. 2.** IR spectra of 0.5 M PC88A in different diluents.

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