



# Reactive extraction of pimelic (heptanedioic) acid from dilute aqueous solutions using trioctylamine in decan-1-ol



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## ABSTRACT

The present study is on the reactive extraction of pimelic acid (heptanedioic acid) from dilute aqueous solutions by trioctylamine (TOA) in decan-1-ol. The equilibrium studies were performed at 298 K and the results were used to calculate the values of distribution coefficient ( $K_D$ ), loading factor ( $Z$ ) and degree of extraction ( $E\%$ ). The maximum  $K_D$  was obtained as 62.34 when initial concentrations of pimelic acid and TOA were 0.038 and 0.2 mol·kg<sup>-1</sup>, respectively. The extraction efficiency was 98.27% under these conditions. Moreover,  $Z$  values between 0.184 and 2.934 were obtained in the ranges of parameters studied. The data presents the formation of 1:1 and 1:2 pimelic acid-TOA solvates in the organic phase. A solvatochromic model (LSER) was applied to the equilibrium data and the  $K_D$  values obtained using the model show a good fit to the experimental outcomes.

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## 1. Introduction

Recently, there has been a growing attention on the production of carboxylic acids using renewable sources by fermentation process [1]. The production method is a green technique compared to chemical synthesis; however, recovery of the target acid from fermentation broth is required. Separation of these organic acids from dilute aqueous solutions is a challenging problem. Several techniques have been tested; however reactive extraction is favored with its critical advantages, e.g., high recovery rates and low energy demand [2–4]. It is a modified version of traditional liquid–liquid extraction technique containing an extractant in the organic phase has the ability to react with the target acid in the aqueous phase. In the literature, there are significant amounts of studies on the reactive extraction of carboxylic acids carried out by various researchers using several extractants [5–17]. Aliphatic amines such as tri-*n*-octyl amine (TOA) [5–12], trioctylmethylammoniumchloride [12–14] and Amberlite LA-2 [15]; and organophosphorus extractants, e.g., tri-*n*-butyl phosphate [11,12,16,17] and tri-octyl phosphine oxide [16], have been widely and efficiently used for the purpose.

In reactive extraction, the separation of the carboxylic acid facilitates with the interaction between the target acid and extractant molecules. The interaction between these two components results in the formation of acid-extractant solvates in the presence of a diluting medium [2]. In addition, the nature of the reaction is reversible which enables easy recovery of the acid and recycling of the organic phase [4,18]. Furthermore, the acids can be selectively recovered from complex acid mixtures by reactive extraction [19–21]. In the recent years, several researchers performed studies on the use of environmentally-friendly organic phase members such as vegetable oils [22,23] and ionic liquids [14,24–26]. Moreover, studies on the preparation of novel extractants were also reported [27–29].

Reactive extraction is a separation technique based on the difference in solubility and distribution of the solute between aqueous and organic phases. Therefore, it is required to know the solubility and distribution of an acid in these phases prior to its recovery from complex solutions such as wastewaters and production media. This information and data will be needed during the design of a recovery process of the target solute.

However, there is a limited number of studies on pimelic (heptanedioic) acid ( $pK_{a1} = 4.41$ ) in the literature. Ogata et al. studied on production of pimelic acid by several types of microorganisms from azelaic acid [30]. Bretti et al. investigated the

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solubility of pimelic acid in several types of aqueous salt solutions such as  $(C_2H_5)_4NI$ ,  $(CH_3)_4NCl$ , and  $NaCl$  and calculated the activity coefficients of pimelic acid [31]. Li and co-workers reported thermodynamic analysis for solubility of pimelic acid in several ionic liquids, such as  $[EMIM][HSO_4]$ ,  $[PMIM]Br$ ,  $[i-PMIM][HSO_4]$ ,  $[BMIM]Br$ , and  $[BMIM][HSO_4]$ . Using the experimental results, the values of enthalpy and the entropy at different temperatures were calculated for each ionic liquid [32]. As can be seen, even there are reports on the solubility of pimelic acid in various types of aqueous and organic solutions; there is no study on the recovery of pimelic acid in the literature yet.

In this study, it is intended to fill an important gap in the literature on the recovery of pimelic acid. To the best of our knowledge, this is the first study on both physical and reactive extraction of pimelic acid from aqueous solutions. In this respect, decan-1-ol and trioctylamine (TOA) were chosen as diluent and amine extractant, respectively.

## 2. Theory

It is well known that only the undissociated portion of the carboxylic acids can form ion pairs with the amine based extractants. The ion pair formation (Eq. (1)) between the undissociated pimelic acid ( $H_2P$ ) and the extractant (B) occurs at the interface and organic phase.



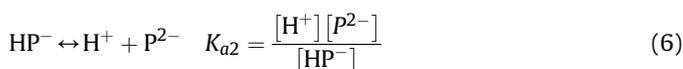
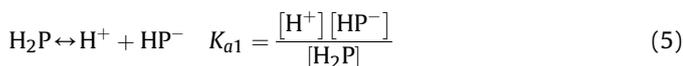
$$K_E = \frac{\overline{(H_2P)_m(B)_n}}{[H_2P]^m [B]^n} \quad (2)$$

The distribution coefficient ( $K_D$ ) is calculated using the Eq. (3), where  $C_{H_2P}$ , and  $\bar{C}_{H_2P}$  represent total acid concentration in the aqueous phase and organic phase, respectively. The amount of acid-extractant complex in the organic phase at equilibrium is shown by  $\overline{(H_2P)_m(B)_n}$ . The degree of extraction ( $E\%$ ) is calculated using Eq. (4).

$$K_D = \frac{\bar{C}_{H_2P}}{C_{H_2P}} = m \frac{\overline{(H_2P)_m(B)_n}}{C_{H_2P}} \quad (3)$$

$$E\% = \frac{\bar{C}_{H_2P}}{C_{H_2P,0}} \quad (4)$$

Since it is a dicarboxylic acid, pimelic acid has two dissociation constants (Fig. 1). The dissociation equations of pimelic acid in the aqueous phase are given in Eqs. (5) and (6):



Therefore, the total pimelic acid concentration in the aqueous

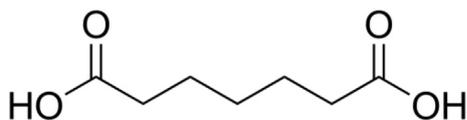


Fig. 1. The chemical structure of pimelic acid.

phase ( $C_{H_2P}$ ) can be expressed by the summation of the undissociated and dissociated acids in the aqueous phase (Eq. (7)). Since the pH values of the aqueous phases were in the range of less than the  $pK_{a2}$  (5.58) of pimelic acid, the dominant forms in the aqueous phase were accepted to be  $[H_2P]$  and  $[HP^-]$ . Thus, dissociation of second carboxylic in pimelic acid was not taken into consideration. Equation (8) was derived by using Eqs. (5) and (7) to determine undissociated acid concentration.

$$C_{H_2P} = [H_2P] + [HP^-] + [P^{2-}] \quad (7)$$

$$[H_2P] = \frac{C_{H_2P}}{\left(1 + \frac{K_{a1}}{[H^+]}\right)} \quad (8)$$

In Eqs. (2) and (3), the concentration of the acid–amine complex formed by ion pair formation was represented as  $\overline{(H_2P)_m(B)_n}$ . Hence, the free amine concentration in the organic phase at equilibrium can be calculated using Eq. (9).

In Eqs. (2) and (3), the concentration of amine molecules formed ion pair with the extracted acid molecules was represented as  $\overline{(H_2P)_m(B)_n}$ . Hence, the free amine concentration in the organic phase at equilibrium can be calculated using Eq. (9).

$$[\bar{B}] = [\bar{B}]_0 - n \overline{(H_2P)_m(B)_n} \quad (9)$$

## 3. Materials and methods

Pimelic acid (purity, >98%), ( $pK_{a1} = 4.41$  and  $pK_{a2} = 5.58$ ) trioctylamine (TOA, purity, 95%) and decan-1-ol were supplied from Alfa Aesar and used in the equilibrium experiments without any pretreatment. The list of the chemicals used in this study is given in Table 1. The aqueous solutions were prepared by dissolving pimelic acid (0.038–0.188 M) in ultra-high pure water obtained from Millipore Milli-Q Water System. The initial concentrations of the extractant (TOA) dissolved in decan-1-ol were changed from 0.05 to 0.20 M (0.021–0.085 wt%). Equal volumes (10 mL) of aqueous and organic solutions were equilibrated in an 100 mL erlenmeyer by shaking (Jeiotech) at 298 K for 2 h. The preliminary experiments show that this is sufficient to reach the equilibrium. After obtaining the equilibrium, the mixture of the phases were settled for an hour to separate the phases. In high concentrations of TOA, the separation with only settling was difficult. Therefore we used a centrifuge to separate the phases. The aqueous phase was carefully removed from the system to be analyzed.

Before and after the extraction experiments, the aqueous phases were analyzed for pimelic acid concentration using fresh NaOH solution (0.01–0.1 N) as titrant and phenolphthalein as indicator. The amount of pimelic acid in the organic phase was determined by mass balance. The reproducibility of the data was observed to be  $\pm 1\%$  of accuracy. All the organic phase components have poor water solubility and the amount of water transferred with pimelic acid from aqueous to organic phase was neglected due to its insignificant amount.

Table 1

The chemicals used in the present study. The reported purities were stated by the suppliers and that the samples were not further purified.

Compound	Source	Purity
Pimelic acid	Alfa Aesar	>98%
Trioctylamine	Alfa Aesar	95%
Decan-1-ol	Alfa Aesar	98%

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