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# Separation of valeric acid from aqueous solutions by reactive extraction using 1-hexyl-3-methylimidazolium hexafluorophosphate

Nilay Baylan

*Department of Chemical Engineering, İstanbul University-Cerrahpaşa, Avcılar 34320, İstanbul, Turkey, Tel. +90 212 473 70 70; Fax: +90 212 473 71 80; email: nilay.baylan@istanbul.edu.tr*

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**ABSTRACT**

The objective of this study is to examine separation of valeric acid from aqueous solutions using an imidazolium-based ionic liquid and tributyl phosphate (TBP). As an imidazolium-based hydrophobic ionic liquid, [HMIM][$PF_6$] (1-hexyl-3-methylimidazolium hexafluorophosphate) was used. TBP is utilized as an extractant in ionic liquid. An experimental examination of reactive extraction and physical extraction was performed and compared with each other. The effects of different parameters on separation such as extractant (TBP) concentration in [HMIM][$PF_6$] (0–1.00 mol $L^{-1}$), valeric acid concentration (0.10–0.30 mol $L^{-1}$) and temperature (25°C–65°C) were investigated. In order to appraise the characteristics of extraction operation, extraction efficiencies ($E$), distribution coefficients ($D$) and loading factors ($Z$) were calculated by using the experimental data. This extraction study has shown that TBP in ionic liquid [HMIM][$PF_6$] is an efficient extractant for valeric acid separation and the extraction efficiency has increased considerably as compared with the physical extraction. It was obtained that 1 mol $L^{-1}$ TBP in [HMIM][$PF_6$] extracts more than 87% of valeric acid from water.

*Keywords:* Valeric acid; Reactive extraction; Ionic liquid; Tributyl phosphate

## 1. Introduction

Carboxylic acids are frequently present in wastewater or effluents of chemical facilities or can be manufactured as a by-product in the manufacturing of chemical reactions. Valeric acid, pentanoic acid or short chain straight fatty acid, is extensively used in variety of industrial applications' such as lubricants, plasticizers, biodegradable solvents, perfumes, flavors, and pharmaceuticals. It is also utilized as a monomer in the polymerization processes. It is a by-product in the production of adipic acid and it must be separated during the purification [1,2].

Various separation processes such as solvent extraction [3–5], adsorption [6–8], and membrane separation [9–11] have been utilized for valeric acid separation from aqueous solutions. On the other hand, reactive extraction is broadly used for carboxylic acid separation from aqueous solutions such as fermentation broths and industrial waste streams. Reactive extraction can be defined as a process in which solvent extraction occurs simultaneously with the chemical complexation [9]. Reactive extraction of acids from aqueous solutions for relatively dilute solutions provides a higher selectivity and separation efficiency. This separation method also requires smaller equipment [2,12].

Organophosphorous compounds, such as tributyl phosphate (TBP), trioctylphosphine oxide (TOPO), and aliphatic amines such as trioctylamine (TOA), tributylamine (TBA) have been widely utilized as extractants for the removal and recovery of carboxylic acids from aqueous solutions. These compounds show a high selectivity and solvent capacity [2,9]. The conventional organic solvents such as ketones, ethers, alcohols, and aliphatic hydrocarbons are commonly used as a diluent in reactive extraction [12]. In the literature survey, the reactive extraction systems (extractants in

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diluents) including Amberlite LA-2 and TBP in toluene [13], TOA in methyl isobutyl ketone (MIBK), 1-octanol, hexane, tetrachloromethane, and chloroform [14] and TOA in 1-octanol, MIBK, tetrachloromethane [15] were investigated for the removal of valeric acid from aqueous solutions. These organic solvents cause environmental pollution because they have toxic, flammable, and volatile properties. Thus, the search for a novel solvent is a key trend in the extraction. In this sense, ionic liquids are considered as alternative solvents to replace conventional organic solvents for extraction processes [16–18].

Ionic liquids are molten salts of a combination of particular cations and anions. The cations are organic such as imidazolium, phosphonium, pyrrolidinium, pyridinium, sulfonium, and ammonium. The anions can be organic or inorganic such as hexafluorophosphate, bis(trifluoromethanesulfonyl)imide, tris(trifluoromethylsulfonyl)methide, tetrafluoroborate, nitrate, acetate, and halides. The anionic group determines the hydrophobic characteristic of the ionic liquid. The hydrophobic anions extensively used are bis (trifluoromethylsulfonyl)imide, hexafluorophosphate, tetracyanoborate, and tris(trifluoromethylsulfonyl)methide. They have remarkable features including low-vapor pressure, good thermal stability, non-flammable, highly tunable, and good solubility for various compounds. Taking into account significant features of ionic liquids, they are also called "green solvents" and have received increasing attention as alternative for green separation processes [16,19,20].

Several studies related to the reactive extraction of valeric acid by using traditional extraction solvents have been conducted aforementioned above, but there is no research about the use of ionic liquids as a solvent in valeric acid extraction. In view of this, separation of valeric acid from aqueous solutions by using ionic liquid [HMIM][$PF_6$] as a green solvent and TBP as an extractant was investigated in this study. This paper also focuses on the effects of various parameters on separation including initial valeric acid concentration, TBP concentration in ionic liquid, and temperature. This work also presents the values of extraction efficiencies, distribution coefficients, and loading factors.

## 2. Theory

The extraction of valeric acid (HA) using extractant TBP ($E$) can be represented with the reaction below [21]:

$$\mathrm{pHA_{aq}} + \mathrm{qE_{org}} \leftrightarrow \left(\left(\mathrm{HA}\right)_p - \left(E\right)_q\right)_{\mathrm{org}} \tag{1}$$

where HA signifies the nondissociated acid in aqueous phase, $E$ represents extractant in organic phase, and $(\mathrm{HA})_p$–$(E)_q$ symbolizes acid–extractant complex in organic phase.

Acid molecules in aqueous phase bind to TBP molecules in organic phase, acid–TBP complexes are formed. This mechanism is also illustrated in Fig. 1.

Distribution coefficient ($D$) is characterized as the acid extracted from aqueous phase into organic phase as follows [22]:

$$D = \frac{C_{A,\mathrm{org.}}}{C_A} \tag{2}$$

Extraction efficiency ($E$) is described as the proportion of extracted acid to initial acid represented as below [22]:

$$E = \left(1 - \frac{C_A}{C_{A0}}\right) \times 100 \tag{3}$$

The loading factor ($Z$) is specified as the concentration of acid in the organic phase divided by the concentration of extractant in the organic phase. It is expressed in the following equation [22]:

$$Z = \frac{C_{A,\mathrm{org.}}}{C_{E,\mathrm{org.}}} \tag{4}$$

where $C_{A0}$ (mol $L^{-1}$) is the concentration of initial acid in the aqueous phase, $C_A$ (mol $L^{-1}$) is the concentration of acid in the aqueous phase at the end of the extraction, and $C_{A,\mathrm{org.}}$ (mol $L^{-1}$) is the concentration of acid in the organic phase at the end of the extraction. $C_{E,\mathrm{org.}}$ (mol $L^{-1}$) is the extractant concentration in the organic phase.

## 3. Materials and methods

The valeric acid (Fluka, >99%) solutions were prepared by using distilled water. The organic solutions were prepared by the dissolution of TBP (Sigma-Aldrich, >99%) in ionic liquid [HMIM][$PF_6$] (Iolitec, >99%). The extraction experiments were conducted by using a thermostatic water bath shaker (Nüve ST 30). Equal volumes (2 mL) of aqueous valeric acid and organic solutions were added to glass flasks and were shaken for the determined optimum time (60 min) in the water bath with a rate of 150 rpm. After that, they were centrifuged in 3,000 rpm for 10 min to separate phases. The concentrations of valeric acid in the aqueous phases were analyzed with an automatic titrator (SI Analytics, Schott Titroline) using NaOH solution. The concentrations

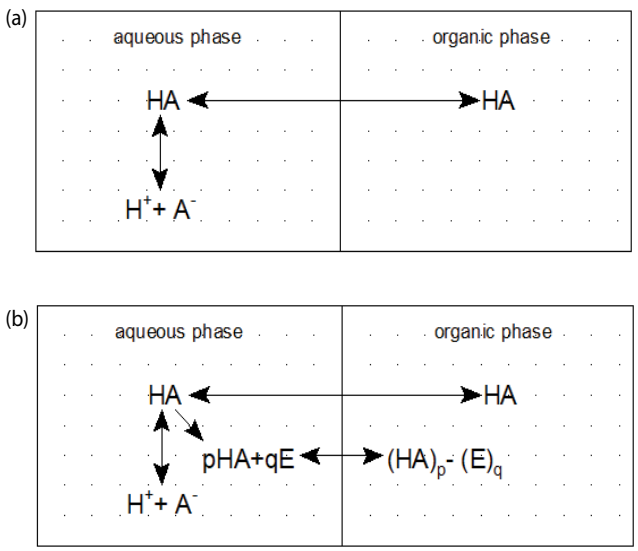


Fig. 1. (a) Physical extraction and (b) reactive extraction mechanism of carboxylic acid from aqueous solution.

of valeric acid in the organic phases were specified by means of the material balance.

## 4. Results and discussion

### 4.1. Determination of equilibrium extraction time

The extraction experiments were performed for the determination of equilibrium time by using valeric acid solution of 0.30 mol $L^{-1}$ and ionic liquid [HMIM][$PF_6$] and 1.00 mol $L^{-1}$ TBP in [HMIM][$PF_6$] at 25°C. The obtained experimental results of equilibrium time for valeric acid extraction are plotted in Fig. 2. As can be seen from the figure, the equilibrium time for valeric acid extraction was determined as 60 min.

### 4.2. Effect of TBP concentration

The initial valeric acid concentration in aqueous phase was 0.30 mol $L^{-1}$ (=3.06% w/w). Initial extractant (TBP) concentrations in [HMIM][$PF_6$] varied between 0 and 1.00 mol $L^{-1}$ to determine the TBP concentration effect on valeric acid extraction. The extraction temperature was 25°C. The effect of TBP concentration on physical extraction and reactive extraction for valeric acid was shown in Table 1. As shown in the table, a substantial quantity of valeric acid was extracted from aqueous solutions by using TBP. When TBP is utilized as an extractant, the extraction degree of acid increases.

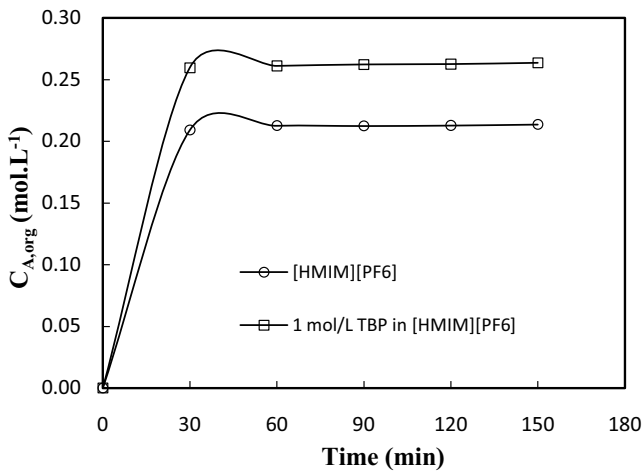


Fig. 2. Effect of equilibrium time for valeric acid extraction.

Table 1
Effect of TBP concentration on the physical extraction and reactive extraction of valeric acid

| $C_{E,org.}$ (mol $L^{-1}$) | $C_{A,org.}$ (mol $L^{-1}$) | $C_A$ (mol $L^{-1}$) | $D$ | $Z$ | $E$ (%) |
|---|---|---|---|---|---|
| 0.00 | 0.213 | 0.087 | 2.45 | – | 71.00 |
| 0.27 | 0.235 | 0.065 | 3.62 | 0.87 | 78.33 |
| 0.55 | 0.250 | 0.050 | 5.00 | 0.45 | 83.33 |
| 0.80 | 0.258 | 0.042 | 6.14 | 0.32 | 86.00 |
| 1.00 | 0.261 | 0.038 | 6.87 | 0.26 | 87.29 |

However, at higher TBP concentrations, free TBP concentration is increased more in the organic phase and more acid molecules are extracted from the aqueous phase [17]. The maximum extraction efficiency of valeric acid is 87.29% with TBP concentration in [HMIM][$PF_6$] of 1.00 mol $L^{-1}$. In other words, using TBP increased the extraction efficiency from 71.00% for physical extraction to 87.29% for reactive extraction.

Fig. 3 displays the effect of TBP concentration on extraction efficiency, distribution coefficient and loading factor. It is obvious from Fig. 3 that the extraction efficiency and distribution coefficient increased with increasing TBP concentration in [HMIM][$PF_6$]. These results obtained from this work were further validated by the observations from similar works [23,24]. However, Fig. 3 depicts that the loading factor decreased with the increase in TBP concentration. In this present study, the loading factor decreased from 0.87 to 0.26 with increasing the concentration of TBP in [HMIM][$PF_6$] from 0.27 to 1.00 mol $L^{-1}$ showing that complexes contain more than one phosphate per complex. Overloading, loading factor greater than unity, demonstrates that the complexes with more than one acid molecule per phosphate are formed [25]. Therefore, overloading was no observed with all TBP concentrations.

### 4.3. Effect of initial acid concentration

Table 2 demonstrates the effect of initial valeric acid concentration on the physical extraction with [HMIM][$PF_6$] and reactive extraction of valeric acid with TBP in [HMIM][$PF_6$] from aqueous solutions. The effect of initial valeric acid concentration on the extraction efficiency and distribution coefficient can be also seen in Fig. 4. The initial valeric acid concentration of aqueous phase was in range of 0.10–0.30 mol $L^{-1}$. The extraction experiments were carried out at 25°C.

Table 2 and Fig. 4 clearly signify that the initial concentration of valeric acid affects the extraction efficiency and distribution coefficient. As initial valeric acid concentration increased, extraction efficiency and distribution coefficient increased. Furthermore, the use of TBP as an extractant in reactive extraction process (in case of 1 mol $L^{-1}$ TBP in [HMIM][$PF_6$]) resulted in a considerable increase in the extraction efficiency and distribution coefficient for valeric acid reactive extraction as compared with physical extraction. Similarly, İnci and Uslu [26] examined the reactive extraction of citric acid and they reported that the extraction efficiency and distribution coefficient increased with increasing initial acid concentration in aqueous phase.

### 4.4. Effect of temperature

In order to determine temperature effect on the physical extraction and reactive extraction, the valeric acid concentration in the aqueous solution of 0.30 mol $L^{-1}$ (=3.06% w/w) and [HMIM][$PF_6$] or 1 mol $L^{-1}$ TBP in [HMIM][$PF_6$] in the organic solution were used in the experiments. The extraction temperature was range in between 25°C and 65°C.

Table 3 indicates the effect of temperature on the physical extraction and reactive extraction of valeric acid. Moreover, in Fig. 5, the effect of the temperature on the extraction

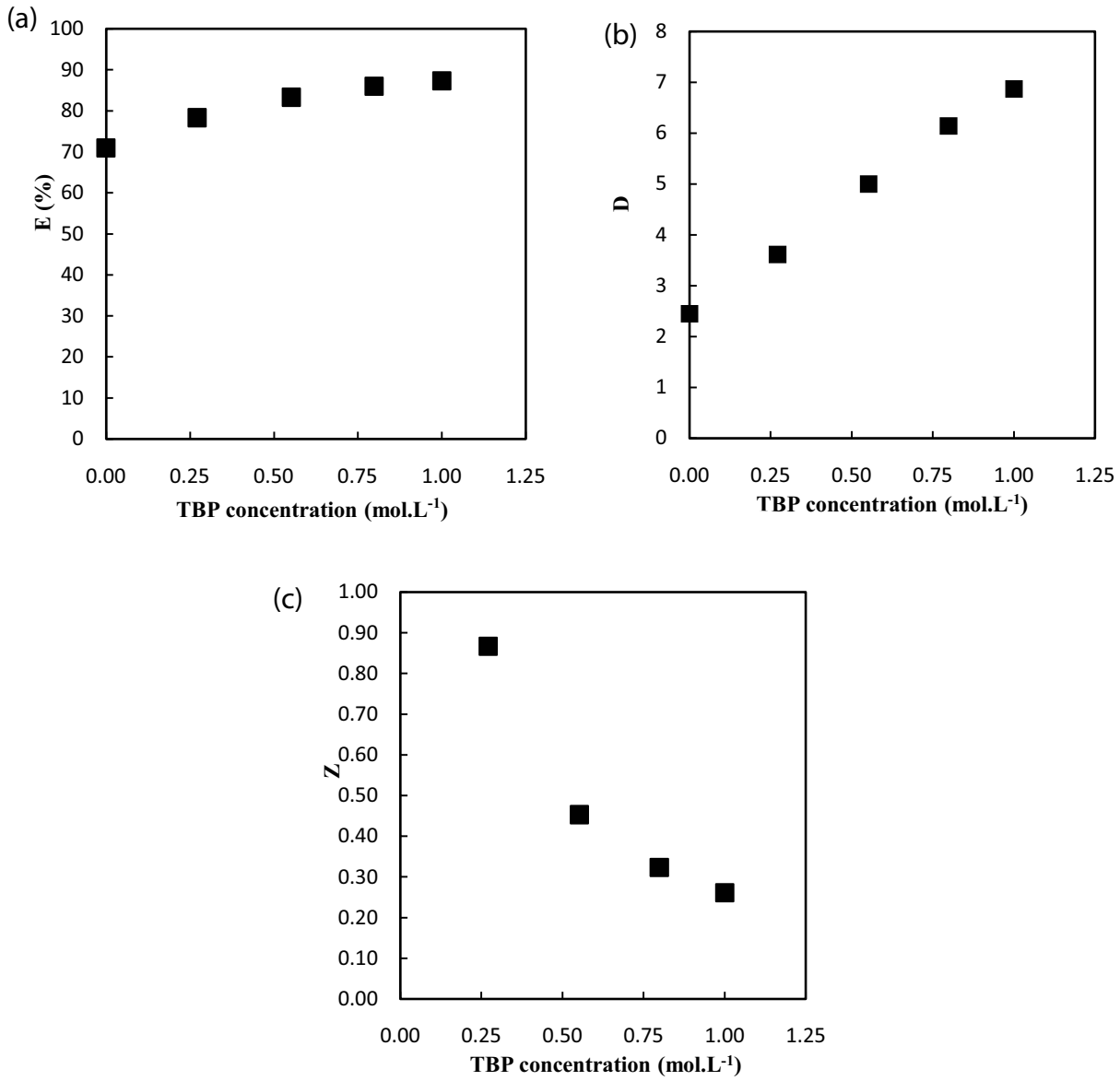


Fig. 3. Effect of TBP concentration on (a) extraction efficiency (*E*), (b) distribution coefficient (*D*), and (c) loading factor (*Z*).

Table 2
Effect of initial valeric acid concentration on the physical extraction and reactive extraction of valeric acid

| $C_{A0}$ (mol L$^{-1}$) | $C_{E,org.}$ (mol L$^{-1}$) | $C_{A,org.}$ (mol L$^{-1}$) | $C_A$ (mol L$^{-1}$) | *D* | *Z* | *E* (%) |
|---|---|---|---|---|---|---|
| 0.10 | 0.00 | 0.050 | 0.045 | 1.11 | – | 52.63 |
| | 1.00 | 0.070 | 0.030 | 2.32 | 0.07 | 69.91 |
| 0.15 | 0.00 | 0.088 | 0.057 | 1.54 | – | 60.69 |
| | 1.00 | 0.115 | 0.032 | 3.59 | 0.12 | 78.23 |
| 0.20 | 0.00 | 0.130 | 0.065 | 2.00 | – | 66.67 |
| | 1.00 | 0.163 | 0.032 | 5.09 | 0.16 | 83.59 |
| 0.25 | 0.00 | 0.168 | 0.077 | 2.18 | – | 68.57 |
| | 1.00 | 0.210 | 0.035 | 6.00 | 0.21 | 85.71 |
| 0.30 | 0.00 | 0.213 | 0.087 | 2.45 | – | 71.00 |
| | 1.00 | 0.261 | 0.038 | 6.87 | 0.26 | 87.29 |

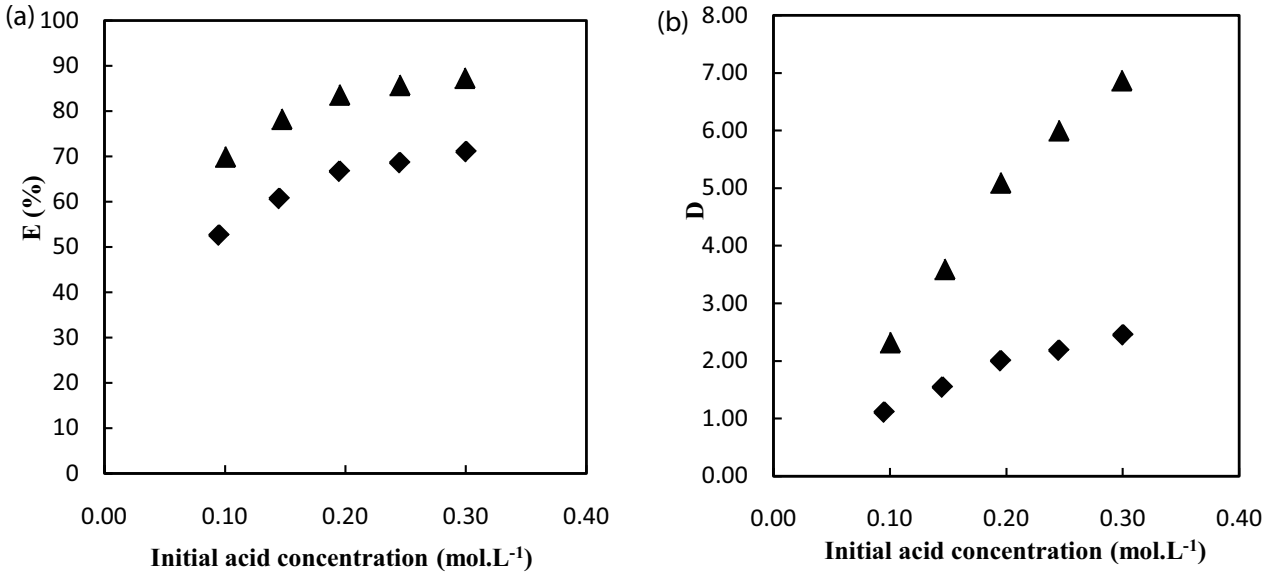


Fig. 4. Effect of initial valeric acid concentration on (a) extraction efficiency (*E*) and (b) distribution coefficient (*D*). ◆ [HMIM][$PF_6$] ▲ 1 mol $L^{-1}$ TBP in [HMIM][$PF_6$].

Table 3
Effect of temperature on the physical extraction and reactive extraction of valeric acid

| *T* (°C) | $C_{E,org.}$ (mol $L^{-1}$) | $C_{A,org.}$ (mol $L^{-1}$) | $C_A$ (mol $L^{-1}$) | *D* | *Z* | *E* (%) |
|---|---|---|---|---|---|---|
| 25 | 0.00 | 0.213 | 0.087 | 2.45 | – | 71.00 |
| | 1.00 | 0.261 | 0.038 | 6.87 | 0.26 | 87.29 |
| 45 | 0.00 | 0.216 | 0.084 | 2.57 | – | 72.00 |
| | 1.00 | 0.262 | 0.037 | 7.08 | 0.26 | 87.63 |
| 65 | 0.00 | 0.219 | 0.080 | 2.74 | – | 73.24 |
| | 1.00 | 0.263 | 0.036 | 7.31 | 0.26 | 87.96 |

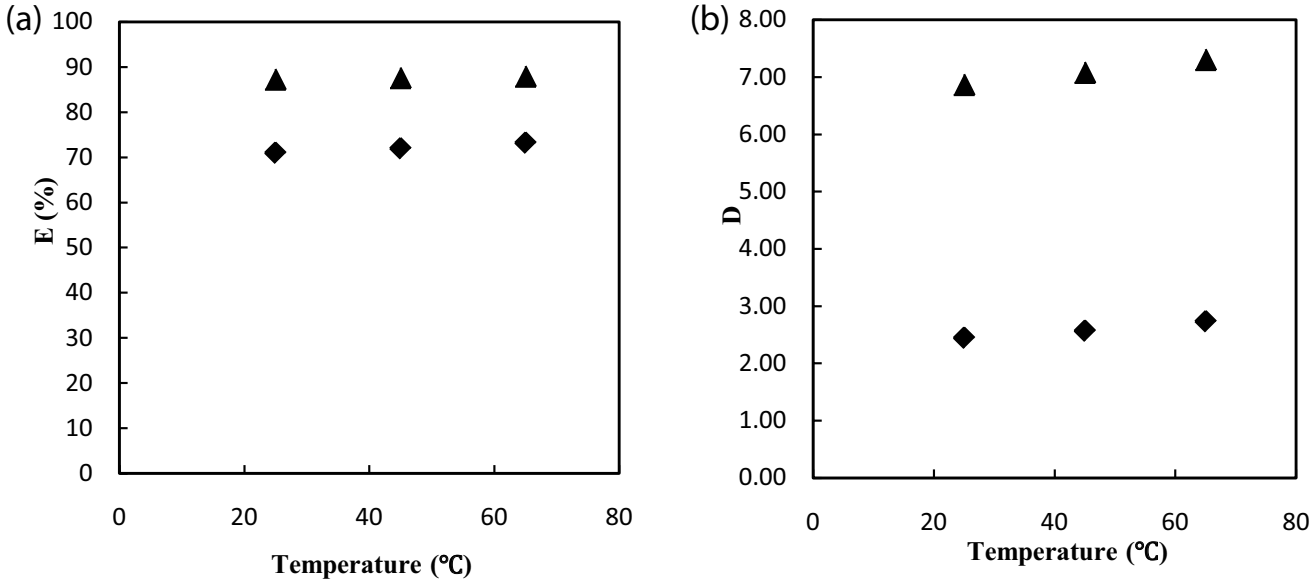


Fig. 5. Effect of temperature on (a) extraction efficiency (*E*) and (b) distribution coefficient (*D*). ◆ [HMIM][$PF_6$] ▲ 1 mol $L^{-1}$ TBP in [HMIM][$PF_6$].

efficiency and distribution coefficient is presented. From Table 3 and Fig. 5, it can be seen that the change in temperature has no significant effect on both extraction efficiency and distribution coefficient over the investigated temperature range. Further, it is obvious from Fig. 5 that the use of TBP in organic phase is more effective parameter than temperature. When similar studies are examined in the literature, Marták and Schlosser [27] investigated lactic acid extraction with phosphonium ionic liquids and they reported that the distribution coefficient does not change or only slightly increased with increasing temperature. Kertes and King [28] examined lactic acid extraction using traditional solvents such as alcohols, ketones, and ether, and they found that the temperature increasing caused only a very slight effect on the distribution coefficient.

## 5. Conclusion

The goal of present work is to examine the extractability of valeric acid from aqueous solutions using an imidazolium-based ionic liquid [HMIM][$PF_6$] and TBP. Ionic liquid [HMIM][$PF_6$] and TBP were successfully employed to the separation of valeric acid from aqueous solutions. An elaborate investigation of reactive extraction and physical extraction was performed. Especially, the effects of TBP concentration, initial valeric acid concentration, and temperature on the separation were detected. The experimental results were evaluated by means of the extraction efficiency, distribution coefficient, and loading factor. It was determined that the extraction efficiency and distribution coefficient increased with increasing initial valeric acid concentration in aqueous phase and TBP concentration in ionic liquid. Moreover, it was also stated that the loading factor decreased with increasing TBP concentration in organic phase. This work has shown that ionic liquid [HMIM][$PF_6$] as a green solvent can be successfully employed in physical extraction process. It has also been found that valeric acid can also be removed effectively from aqueous solutions by physical extraction using [HMIM][$PF_6$]. Besides, the reactive extraction using TBP in [HMIM][$PF_6$] has considerably increased the separation efficiency of valeric acid as compared with the physical extraction.

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