Extraction of Valeric acid using phosphate salts and PEG in aqueous two phase systems

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Abstract

The application of aqueous two phase systems (ATPSs) is a powerful and efficient method to extract metal ions, as well as biomolecules such as proteins, enzymes, organic acids and antioxidants. In this study, the distribution and phase equilibrium of separation of valeric acid or pentanoic acid ($C_5H_{10}O_2$) in ATPS has been investigated. Valeric acid is used in the perfume industry, the production of synthetic lubricants, agriculture and pharmaceuticals. Distribution coefficient and efficiency of Valeric acid in the presence of PEG2000 and PEG8000 and phosphate salt such as sodium di-hydrogen phosphate, di-potassium hydrogen phosphate and di-ammonium hydrogen phosphate at two different temperatures which are 25 ° C and 35 ° C have been reported. The effect of salt type, temperature, pH and salt concentration have been studied. It was observed that as the temperature and pH decreases, the partition coefficient and efficiency of Valeric acid increase. By increasing salt concentration and molecular weight of polymer, the partition coefficient and efficiency of Valeric acid were decreased. In addition, Sodium di-hydrogen phosphate also has higher efficiency of extraction (60% at 25 °C and PEG2000) relative to other phosphate salt.

Keywords: Aqueous two phase systems, Valeric acid, Distribution coefficient, Phosphate salts

Introduction

investigation of separation processes is one of the most crucial issues in the chemical engineering, and also in various industry such as biotechnology, pharmacy, food and etc. currently, ATPSs are widely used in separation and purification processes. ATPSs are formed when the solutions of two hydrophilic materials (polymer-salt or alcohol-salt) are mixed together and their concentration exceeds from certain value [1]. Each phase is enriched with one of the solutes, and both phases have a

high content of water[2,3]. Generally, salt which are used in ATPS procedure are inorganic salts like sulfates or phosphates with different cations (such as sodium, potassium, or ammonium) [4,5], organic salts like citrates[6-12], tartrates [13-15], and others[14,16,17]. Polymer-salt systems have low viscosity and are separated in a shorter time[18,19]. Valeric acid or Pentanoic acid is a straight chain alkyl carboxylic acid used in the industry with the chemical formula $C_5H_{10}O_2$, which has an unpleasant odor. The main usage of valeric acid is in
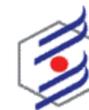
the synthesis of its ester. Due to the production of volatile ester from valeric acid, it converts to a very palatable substance [20, 21].

In this research, separation of valeric acid in ATPSs was examined by using phosphate salts and polyethylene glycol. Besides, effect of diverse factors on the distribution coefficient and efficiency of valeric acid have been evaluated at T=25 to 35 ° C and pH =5 to 8.

Experimental
Materials
K_2HPO_4, $(NH_4)_2HPO_4$, NaH_2PO_4 , PEG2000, PEG8000 and valeric acid were purchased with the highest purity from Merck. In addition, at all steps of the experiment, deionized water was used.

Method
In this experiment, certain amount of phosphate salts with (25, 30, 35 and 40% w/w), PEG2000, PEG8000 and valeric acid were poured into the beakers, separately. Then, contents were mixed for an hour. Finally, beakers were put into incubator at 25 and 35°C for 3 hour. Besides, contents of beakers were transferred to the centrifuge tube, so that the volume of up and down phase were determined. 1cc of samples were taken from up and down phases with syringe and transferred to flask. In order to determine the amount of acid in both phases, titration was utilized. In this proceed, one drop of phenolphthalein as indicator was added to the flask and titrated with 0.1 molar NaOH.

Anaytical Methods
The results were discussed by the distribution coefficient (K) and percentage of extraction (%Y) as follows. In the relations below, C_t , C_b , V_t , V_b and V_r are the concentration of valeric acid in the up and down phases, up and down and the residual volume respectively[22].

$$K = \frac{C_t}{C_b} \qquad (1)$$

$$V_r = \frac{V_t}{V_b} \qquad (2)$$

$$\%Y = \frac{K \times V_r}{1 + K \times V_r} \times 100 \qquad (3)$$

Results and discussion
Effect of salt concentration and temperature
In two-phase systems, salts have a different tendency to up and down phases. Non-symmetric salt partition in these systems in two phases causes the valeric acid to be split into two phases and thus effects on the separation factor. In ATPS which is generated by polymer and salt, inequality responses of salt in the up and down phase creates two separate ionized
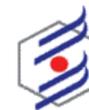
atmospheres in each phase. Finally, with introducing low amount of acid into the ATPS, it is encountered with two separate ion atmospheres. Thus, tendency of acid to these two phases is not the same. As a result, the concentration of salt may lead to increase or decrease the partition coefficient or percentage of extraction [23]. Figures 1 to 3 express effect of salt concentration for K_2HPO_4, $(NH_4)_2HPO_4$ and NaH_2PO_4 on extraction of valeric acid in ATPSs. Temperature can have various influence on partition coefficient in various systems. At high temperatures, due to the change in the conformation of polyethylene glycol and also reduction in specific interactions of polyethylene glycol with acid, the extraction of acid is decreased. In addition, low temperatures may increase the separation coefficient due to the salting- out phenomenon [24]. Figures 1 to 3 express effect of temperature for K_2HPO_4, $(NH_4)_2HPO_4$ and NaH_2PO_4, on extraction of valeric acid in ATPSs.
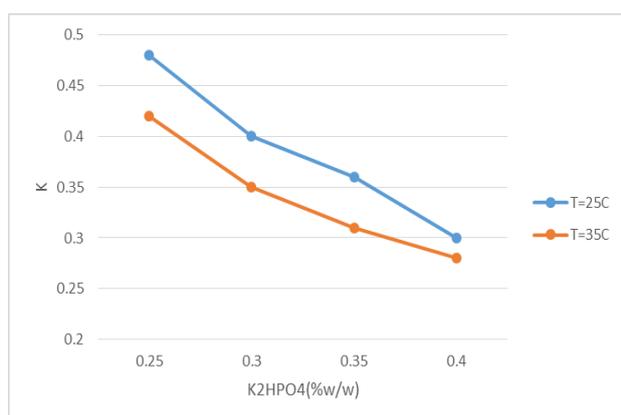

Fig 1 . Diagram of Distribution coefficient for K_2HPO_4 at 25 and 35°C
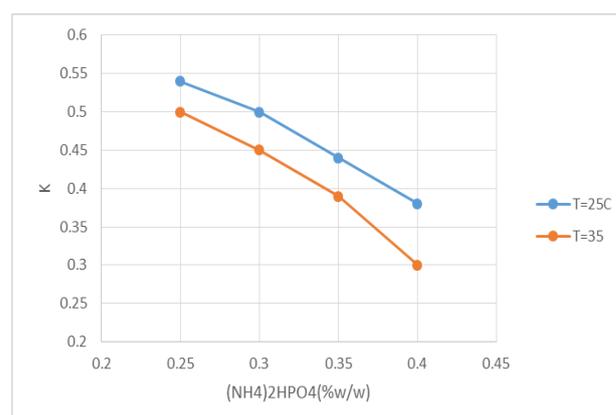

Fig 2 . Diagram of Distribution coefficient for $(NH_4)_2HPO_4$ at 25 and 35°C
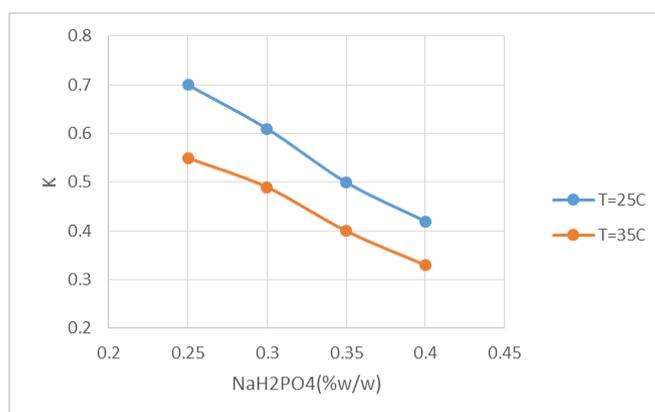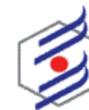

Fig 3 . Diagram of Distribution coefficient for NaH_2PO_4 at 25 and 35°C

Effect of pH and molecular weight of polymer
As the pH increases, acid tend to move in bottom phase. By increasing the pH, the attraction decreases between the polymer and the water so that water moves to a salt-rich phase. As a result, the volume of top phase decreases and the volume of bottom phase increases, which causes to reduces the Distribution coefficient and the efficiency extraction of valeric acid[25]. Table 1 shows effect of pH for K_2HPO_4, $(NH_4)_2HPO_4$ and NaH_2PO_4, on extraction of Valeric acid in ATPSs.

Table 1: Distribution coefficient and efficiency extraction for phosphate salts in different pH

salt	pH=5				pH=8			
	PEG2000		PEG8000		PEG2000		PEG8000	
	K	%Y	K	%Y	K	%Y	K	%Y
K_2HPO_4	0.55	40.7	0.42	35	0.32	37.5	0.29	31
$(NH_4)_2HPO_4$	0.61	48	0.5	40.5	0.41	42.5	0.34	33.5
NaH_2PO_4	0.82	60	0.61	54	0.56	50	0.5	41

Effect of the type of salt
When ions of salt have a high Gibbs free energy, they can hydrate more molecules of water and show a higher degree of salting-out. Finally, number of water molecules remains to hydrate the valeric acid molecules, which results in the accumulation and evolution of highly polymerized high valeric acid molecules [23]. According to figures 4, Gibbs energy hydration for NaH_2PO_4 is higher than two other salts so that, it has a higher percentage of extraction.
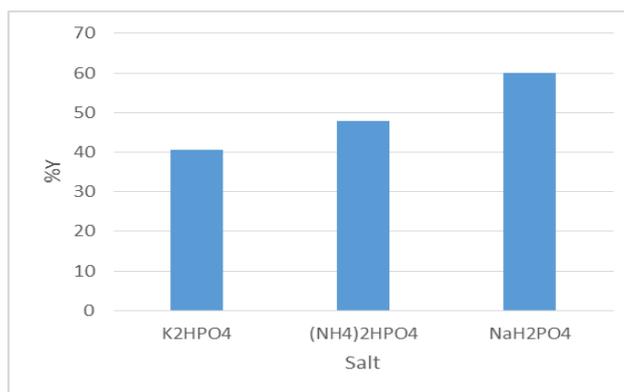

Fig 4 . Diagram of efficiency extraction for phosphate salts at 25°C and PEG2000

Conclusions
In this work, valeric acid extraction was accomplished in ATPS and process parameters such as salt concentration, temperature, pH, molecular weight of polymer and the type of salt have been evaluated in PEG/phosphate systems. The lower the MW, the higher K achieved. It was observed that the length of carbon chains were extended and hydrophobicity of polymer was increased, so that particles tend to salt rich phase. Ultimately, Distribution coefficient and percentage of extraction were decreased. Concentration of salt had the important effect on the distribution coefficient and extraction efficiency. the effect of salt concentration on distribution coefficient and extraction efficiency for NaH_2PO_4 at T=25°C, displayed that the

lowest salt concentration (25%w/w) lead to to phase volume ratio was declined, so that the separation parameters were increased. Partition of valeric acid was extremely affected by temperature. Consequently, T=25°C was the optimal choice. The pH had drastic influence on the partition of the valeric acid. It is observed that pH=5 was a suitable value in PEG/phosphate systems.

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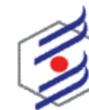
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