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Green Chemistry For Citric Acid Recovery From Bioreactor: Effect Of Temperature

Divya Raheja, Amit Keshav*

**Department of Chemical Engineering, National Institute of Technology (NIT), Raipur,
Chhattisgarh, India.**

***Corres. Author: dr.amitkeshav@gmail.com
Tel.:09630058194**

Abstract: Extraction of citric acid was studied to explain the effect of temperature on the extraction. Temperature is an important parameter for the design of extraction process in terms of the effect of varying temperature of the substrate sources. In the present paper effect of temperature was investigated for the extraction of citric acid using tertiary amine (tri-n-octylamine) in diluent (2-octanol) as the solvent system. Distribution coefficient, equilibrium complexation, constants and loading ratios were found. Decrease of equilibrium complexation constant from 345.86 to 80 l/mol was observed as temperature was increased from 303 K to 353 K, thus suggesting that extraction is exothermic.

Keywords: Extraction, tri-n-octylamine, 2-octanol, equilibrium, temperature.

Introduction

Citric acid is a tri-carboxylic acid widely used in the field of food and beverages, as an acidulant, as well as in pharmaceutical and chemical products. Citric acid palatability and easy access for assimilation have led to its utility as an acid ingredient. Although citric acid can be obtained by chemical synthesis, it is commercially produced by fermentation because of the much lower cost. Low concentration of citric acid (<10%) is achieved in fermentations process for citric acid manufacture. Citric acid is typically purified by a firmly established process known as the method of calcium salt precipitation.

In recent years, reactive extraction processes are gaining lot of importance in response to extreme economic pressure posed by industries as the result of emergence of new processes and decline of existing ones, demand of high purity products with low cost and are environmentally safe production techniques. For the last few decades, there has been intensive work on the reactive extraction for the recovery of carboxylic acid from waste water solutions and fermentation broths. Reactive extraction being a clean and green process, since the extractant for the recovery of the acid can be completely recovered and reused. The simple and cheap operation has created a lot of scope as an efficient recovery process.

The distribution coefficient of citric acid was strongly temperature dependent. That makes it possible to strip the acid into water at a higher temperature. Alamine 336 dissolved in a non-polar diluent was a suitable solvent¹. And the distribution of citric acid between water and amine dissolved in a diluent depended greatly on the choice of diluent². Few studies were done to observe the synergistic extraction of carboxylic acids. The presence of more than one acid in the aqueous phase affects the extraction characteristics. This was demonstrated³, who used solvent extraction and supported liquid membranes for the separation of lactic and citric acids with tri-n-octylamine (TOA) used as the extractant. The extracted citric acid from aqueous solution using a supported liquid membrane⁴. A combination of extraction/re-extraction process using a tertiary amine containing solvent was developed in this regard^{5,6}.

Materials And Method

Citric acid was obtained from Merck Co Ltd. Germany. Tri-n-octylamine (TOA) is commercially available tertiary amine was used as extractant and was supplied by Aldrich Co. India. Sodium hydroxide was used for analysis was purchase from Fisher Scientific and were used without pre-treatment. Aqueous solutions of acid were prepared using distilled water.

Different concentration of citric acid were prepared (0.016, 0.033, 0.066, 0.09, 0.13, 0.16 mol/l). 20ml each of these solution was taken into 100 ml conical flask and different percentage of TOA (10-30%) were added into the contents in each of the conical flask at different temperatures 303-333K. The content of the flask were shaken for 4 hrs at specific temperature and settled for 2 hrs. Citric acid concentration in the aqueous phase was determined by titrating against standard NaOH solution using phenolphthalein as an indicator.

Theory

The extent to which the organic phase can be loaded with citric acid is expressed as the loading ratio. The loading of the extractant z , is defined as the total concentration of acid in the organic phase divided by the total concentration of amine in the organic phases.

$$z = \frac{[H_3A]_{org}}{[R_3N]_{org}} \quad (1)$$

The value of z depends on the extractability of the acid, i.e. strength of the acid-base interaction, and its aqueous concentration. The stoichiometry of the overall extraction reaction depends on the loading ratio in the organic phases, z . If the organic phase is not highly concentrated, ie at very low loading, the (1:1) complex is formed and a plot of $z/(1-z)$ versus acid concentration in aqueous phase is a straight line whose slope gives the complexation constant K_{E1} in Equation (2).

$$z/(1-z) = K_{E(1:1)} [H_3A]_{aq} \quad (2)$$

Result And Discussion

Study of effect of temperature on the extraction with reaction is essential in view of climatic conditions of the various areas in India. At Chattisgarh (India) the winter temperature is 20-30 °C and summer goes to 40-50 °C. Thus, it becomes important to study the performance of reactive extraction process under these temperature conditions. In view of this in the present study effect of temperature on the reactive extraction of citric acid using tri-n-octylamine in 2-octanol was studied. Usually, extraction is an exothermic process and a decrease in extraction is expected as the temperature is increased. However, it can be stated that the decrease in extraction is the function of the extractant and diluent chosen i.e. the extracting medium. Thus, it makes the study of temperature effect important when the process is to be designed. Further, the variation in climate, feed and bioreactor conditions make the study of temperature effect more important.

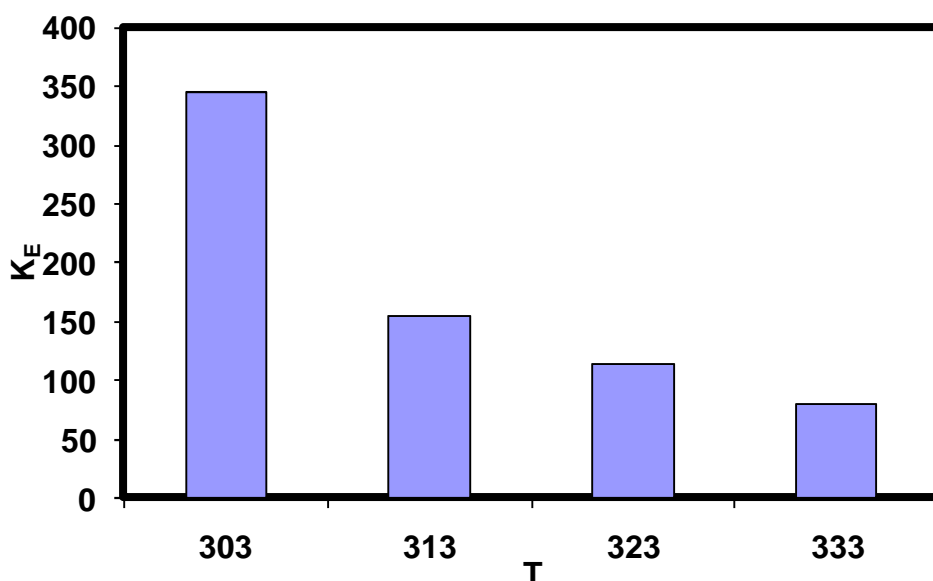


Figure 1: Effect of temperature (303-333 K) on the reactive extraction of citric acid using TOA in 2-octanol.

Figure (1) reported the K_E (1:1) values for extraction of citric acid using TOA in 2-octanol, at $T = 303$ - 333 K. A large decrease in K_E was observed. K_E values decreases from 345.86 to 80 l/mol as temperature was varied from 303-333 K. Thus 77% decrease in K_E was observed. Such a large decrease in K_E suggests that a proper temperature control of the extraction system is desired since it could adversely affect the progress of the reactive extraction process if temperature is varied in the respective range. On the other hand this could be an attractive choice of the regeneration of acid by temperature swing regeneration method, where, extraction with high recovery could be attained at low temperature and by temperature swing to a higher temperature; the acid could be recovered from the organic phase. For a fixed temperature it was found that K_D increases with acid concentration (0.016-0.16). This trend was observed for the entire range of temperatures (303-333K). A slight discrepancy may be accounted due to experimental deviations/errors. For a fixed acid concentration and variable temperatures (303-333 K), K_D values decreases with increase in temperature. These results were in agreement with the trend of K_E .

If the enthalpy and entropy of reaction are assumed to be constant over the temperature range (303-333), the equilibrium complexation constant is related to temperature.

$$\ln K_E = -\frac{H}{RT} + \frac{\Delta S}{R} \quad (3)$$

The above expression indicates that a plot of $\ln K_E$ vs $1/T$ gives a straight line. The more exothermic the reaction, the more sensitive the equilibrium is to changes in the temperature. The slope is proportional to the enthalpy of reaction, and the intercept is proportional to the entropy. Figure (2) shows the plot of $\ln K_E$ vs $1/T$ for the extraction of citric acid using TOA in 2-octanol, when temperature was varied from 303 K to 333 K. The values of enthalpy of reaction (H), and entropy of reaction (S) were found to be $-9463.488 \text{ cal.l/mol}^2$ and $-19.87 \text{ cal.l/Kmol}^2$, respectively.

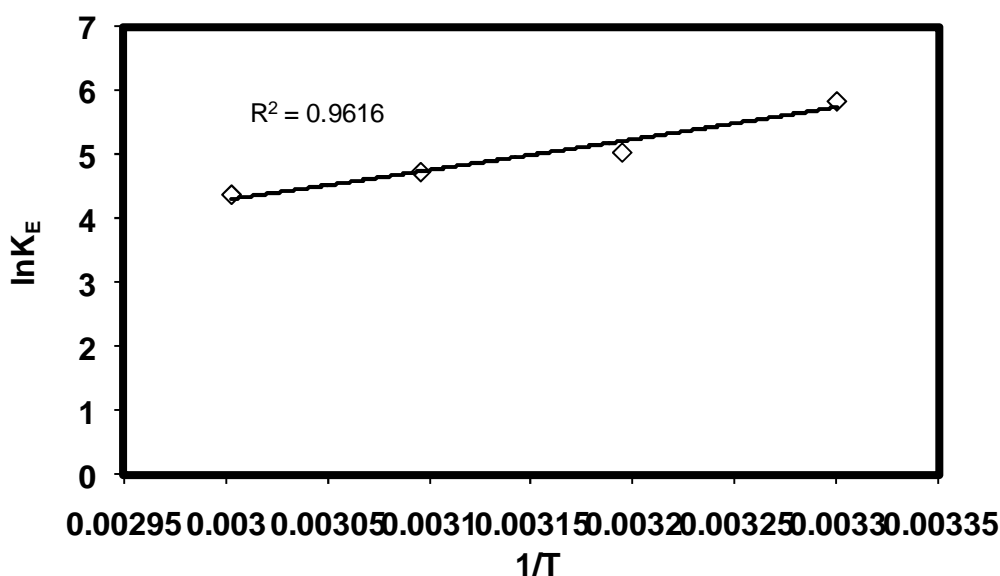


Figure 2: The plot of $\ln K_E$ vs $1/T$ for the extraction of citric acid using TOA in 2-octanol

Extraction of citric acid by extractant is via intermolecular hydrogen bonding or ion exchange of the extractant group with the acid. The extraction of citric acid by extractant-acid complexation is expected to be exothermic and makes the system more ordered. A very high $-\Delta H$ value was obtained for the extraction of citric acid using TOA in 2-octanol. This suggests that the TOA-acid complexation is exothermic. Thus to employ this system for the large scale a proper cooling control strategy is required since this could adversely effect the thermodynamics of the process. Further negative values suggest that the extraction with reaction process is exothermic in nature.

Conclusion

Effect of temperature on the extraction of citric acid using TOA+2-octanol system was studied. K_E values decreases from 345.86 to 80 l/mol as temperature was varied from 303-333 K. Enthalpy of reaction (ΔH), and entropy of reaction (ΔS) were found to be $-9463.488 \text{ cal.l/mol}^2$ and $-19.87 \text{ cal.l/Kmol}^2$, respectively. This suggests that the TOA-acid complexation is higher exothermic in the case of 2-octanol. The results provide an attractive opportunity for temperature swing regeneration method for back recovery of acid from loaded organic phase.

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