ABSTRACT

Extraction of carboxylic acids from dilute aqueous solution using traditional solvents such as ketones, alcohols, ethers, and ester is inefficient because the distribution ratio is rather low. Reactive extraction which exploits reversible chemical complexation is an effective separation process for extraction of carboxylic acids from aqueous streams such as fermentation broths and wastewaters. Considering its solubility in water, cost and availability, tri-n-butyl phosphate (TBP) seems to be an attractive solvent for the extraction of acetic acid from aqueous solution.

The purpose of this experiment is to study the equilibrium of the reactive extraction of acetic acid in aqueous solution with TBP in n-hexane. The parameters studied in this experiment were initial concentration of acetic acid in the aqueous phase, TBP concentration in n-hexane phase, and the extraction temperature. In this experiment, the initial concentration of acetic acid was varied from 0.1 to 0.5 gmol/dm$^3$. The range of initial TBP concentrations in n-hexane was 0.1 to 1.0 gmol/dm$^3$ and the extraction temperature range was 283 to 313 K.

The overall equilibrium constants ($K_{pq}$) for the experiments using TBP concentration ranging from 0.1 to 1.0 gmol/dm$^3$ at the extraction temperature of 293 K are calculated to be 0.1779 to 0.9650. $K_{pq}$ for the experiments at the temperature ranging from 283 to 313 K at the initial concentration of acetic acid of 0.2 gmol/L are found to be 0.1311 to 0.9912. The $K_{pq}$ as a function of temperature ($T$) in K can be expressed as

$$\ln K_{pq} = \frac{5,629}{T} - 19.92$$

with sum of squared error of 0.21.

Keywords: Reactive Extraction, Equilibrium, Acetic Acid, TBP, n-Hexane.

INTRODUCTION

Production of carboxylic acids by fermentation usually produces low concentrations of carboxylic acids in water which is sometimes less than 10% weight (Tamada and King, 1990). Separation, purification and even to concentrate the fermentation products are very difficult because affinities between acids and water are very strong. Separation of acids and water by distillation consumes a lot of energy to evaporate water (Tamada and King, 1990). The classical process to recover a carboxylic acid from a wide variety of dilute aqueous solutions is based on precipitation of the calcium salt upon addition of calcium hydroxide to the acid aqueous solution (Malmary et al., 1997). This method of recovery results low yield of acid crystallization, costly, and unfriendly to the environment (Juang and Huang, 1994).
The carboxylic acids recovery from dilute acid solutions can be conducted by extraction method. Traditional solvents which are usually used are ketone, alcohol, ether and ester. Using traditional solvent is not very effective because its distribution ratio is very low. Regarding to the different strategies of carboxylic acid recovery from dilute solutions, the reactive extraction is one of the best to ensure an increase in the distribution ratio (Juang and Huang, 1997). Many researchers have investigated reactive extraction of carboxylic acids using some extractants. Ricker et al. (1980) investigated the recovery of acetic acid from dilute aqueous industrial streams using solvent extraction with amines. The recovery of acetic acid from dilute aqueous streams using liquid-liquid extraction with tri-n-butyl phosphate as solvent has been studied by Shah and Tiwari (1981). Malmary et al. (1997) have investigated the liquid-liquid equilibria of acetic acid, formic, and oxalic acids between water and tributyl phosphate plus dodecane.

This paper presents the equilibrium of reactive extraction of acetic acid with TBP in \textit{n}-hexane. TBP reacts with acetic acid to form complexes, while \textit{n}-hexane functions to dilute TBP. TBP has an advantage as solvent for use in aqueous extraction due to its negligible solubility in water (Shah and Tiwari, 1981).

\textbf{EXPERIMENTAL}

\textbf{Reagent and Solutions}

Distilled water with the density of 0.9959 \text{g/cm}^3 and viscosity of 0.0089 \text{g/(cm·s)} was used in this experiment. Acetic acid, TBP, \textit{n}-hexane, and other chemicals were supplied by Merck Co. as analytical reagent grade, and all were used without further purification.

\textbf{Experimental Procedure}

The experiments were done for the extraction of acetic acid with pure \textit{n}-hexane and for the extraction of acetic acid with TBP diluted by \textit{n}-hexane. For measuring the distribution ratio of acetic acid in \textit{n}-hexane, the aqueous solution of acetic acid with a fixed concentration and \textit{n}-hexane of equal volume of 50 cm$^3$ were mixed in a flask and shaken at a fixed temperature for one hour to attain the extraction equilibrium. After two phases were separated, acetic acid concentration in the aqueous phase was determined by titration with known concentration of NaOH solution using phenolphthalein as indicator. The concentration of acetic acid in organic phase was calculated by total mass balance of acetic acid. The experimental parameters were temperature and acetic acid initial concentration.

The experiments for the extraction of acetic acid with TBP in \textit{n}-hexane were carried out by shaken of equal volume (50 cm$^3$) of aqueous solution of acetic acid with solution of TBP in \textit{n}-hexane. The experimental procedure was similar to that explained above, with the experimental parameters of temperature, acetic acid initial concentration, and TBP concentrations.
MATHEMATICAL MODELING

Extraction of Acetic Acid with Pure $n$-Hexane

Most carboxylic acids such as acetic acid mainly exist as dimers in organic phase due to the strong intermolecular hydrogen-bonding, especially in the non-polar or lowly polar solvents (Juang and Huang, 1997). On the contrary, in the aqueous phase, they exist mainly as monomers because the intermolecular hydrogen bonding between the acids is destroyed owing to their preferential hydrogen bonding with water molecules (Juang and Huang, 1994; Juang and Huang, 1997).

The reactions in this extraction as the aqueous pH is far less than the dissociation constant of acetic acid ($pK_a = 4.75$) are as follows (Malmary et al., 1997; Juang and Huang, 1997):

Distribution of acetic acid monomer from the aqueous phase to the organic phase.

\[ HA \leftrightarrow \overline{HA}; K_d = \frac{[HA]}{[HA]} \]  

(1)

Dimerization of acetic acid in the organic phase.

\[ 2\overline{HA} \leftrightarrow (\overline{HA})_2; K_2 = \frac{[HA]}{[HA]^2} \]  

(2)

Dissociation of acetic acid in aqueous phase.

\[ HA \leftrightarrow H^+ + A^-; K_a = \frac{[H^+][A^-]}{[HA]} \]  

(3)

The overbar refers to the organic phase. The concentrations of acetic acid in organic phase and aqueous phase at equilibrium are calculated from the following equations:

\[ \overline{[HA]} = \overline{[HA]} + 2\overline{([HA])_2} \]  

(4)

\[ [HA] = [HA] + [A^-] \]  

(5)

The distribution ratio ($D_0$) of acetic acid in the absence of TBP is defined by Eq. (6).

\[ D_0 = \frac{\overline{[HA]}}{[HA]} \]  

(6)

where $\overline{[HA]}$ is the total concentration of acetic acid in the organic phase and $[HA]$ is the total concentration of acetic acid in the aqueous phase at equilibrium.

Substitution of $\overline{[HA]}$ from Eq. (4) and $[HA]$ from Eq. (5) to Eq. (6) we have the following equation:

\[ D_0 = \frac{([HA] + 2([HA])_2)}{[HA] + [A^-]} \]  

(7)

or

\[ D_0 = \frac{(K_d + 2K_2,K_a,[HA])}{(1 + K_d,[H^+])} \]  

(8)

The value of $[HA]$ at Eq. (8) can be obtained from Eq. (5) and at the measured equilibrium pH, that is $[A^-] = [H^+]$, so that:

\[ [HA] = [HA] + [H^+] \]  

(9)

Eq. (8) can be arranged as:

\[ D_0(1 + K_d,[H^+]) = K_d + 2K_2,K_a[HA] \]  

(10)

By plotting $D_0(1 + K_d,[H^+])$ versus $[HA]$, we get the value of $K_d$ as the intercept of the graph and $2K_2,K_d$ as its slope.

Extraction of Acetic Acid with TBP
The extraction of acetic acid with TBP in n-hexane at pH far less than $pK_a$ can be expressed by the following stoichiometry (Juang and Huang, 1997):

$$pHA + qTBP \leftrightarrow (HA)_q(TBP)_p : K_{pq}$$

(11)

where $K_{pq}$ is the extraction equilibrium constant, which is given by Eq. (12).

$$K_{pq} = \frac{[HA]^q[TBP]^p}{[HA]^q[TBP]^p}$$

(12)

The complexation reaction between acetic acid and TBP in the organic phase is expected to be exothermic. Formation of complex makes the system more ordered and thus decreases the entropy ($\Delta S$). Therefore, as the temperature ($T$) is increased, the amount of acetic acid extracted decreases. If the enthalpy ($\Delta H$) and entropy of reaction are assumed to be constant over the temperature range, the following expression:

$$\ln K_{pq} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$

(13)

indicates that a plot of $\ln K_{pq}$ vs $1/T$ gives a straight line (Tamada and King, 1990). The enthalpy of reaction is obtained from the slope, and the intercept is proportional to the entropy.

**RESULTS AND DISCUSSION**

Figure 1 shows the distribution ratio of the extraction of acetic acid with pure $n$-hexane as a function of initial acetic acid concentration in the aqueous solution at four different temperatures. It appears in Figure 1 that at a fixed temperature, the distribution ratio increases as a function of the initial concentration of acetic acid in the aqueous solution. It can be seen from Figure 1 that the distribution ratio decreases as the temperature increases for the experiments at the same initial concentration of acetic acid in the aqueous solution.

![Fig. 1: Effects of initial acetic acid concentration and temperature on the distribution ratio of the extraction of acetic acid with pure $n$-hexane.](image-url)
From the experimental data, then the value of $K_a$ was calculated by Eq. (3) and the values of $K_2$ and $K_d$ were obtained based on Eq. (10). The values of $K_a$, $K_2$, and $K_d$ as a function of temperature are shown in Figure 2. Figure 2 depicts that the change of the value of $K_a$ as a function of the temperature is relatively small. The value of $K_2$ increases as a function of temperature, while the value of $K_d$ is decreased by increasing the temperature.

Figure 3 illustrates the distribution ratio of the extraction of acetic acid with TBP in $n$-hexane as a function of initial acetic acid concentration in the aqueous solution at different TBP concentration in the organic phase at 293 K. It is found that at a fixed TBP concentration, the distribution ratio tends to increase with increasing the initial acetic acid concentration in the aqueous solution. It is also shown in Figure 3 that at the same initial acid concentration, the distribution ratio increased with increasing TBP concentration.

The effect of temperature on the distribution ratio of extraction of acetic acid with TBP in $n$-hexane is shown in Figure 4. The complexation reaction of acetic acid and TBP in the organic phase involve proton transfer or hydrogen bond formation and are therefore expected to be exothermic. Also, formation of a complex makes the system more ordered and therefore decreases the entropy. Thus, as the temperature increases, the amount of acetic acid extracted decreases (Tamada and King, 1990; Juang and Huang, 1997).

Figure 5 reveals the temperature dependence of the equilibrium constant $K_{pq}$. It can be seen at Figure 5 that the extraction of acetic acid with TBP is exothermic. The enthalpy of reaction ($\Delta H$) is obtained from the slope of the graph and it was found to be $-41.40 \text{ kJ/mol}$, and the intercept is proportional to the entropy ($\Delta S$) and it was found to be $-147.99 \text{ J/(mol·K)}$.

![Fig. 2: Values of $K_a$, $K_2$, and $K_d$ as a function of temperature.](image-url)
Fig. 3: Effects of initial acetic acid and TBP concentrations on the distribution ratio of the extraction of acetic acid with TBP in n-hexane at 293 K.

Fig. 4: Effect of temperature on the distribution ratio of extraction of acetic acid with TBP in n-hexane at the TBP concentration of 0.2 mol/dm³.
Fig. 5: Temperature dependence of the equilibrium constant $K_{pq}$.

CONCLUSIONS

The reactive extraction of acetic acid from aqueous solution with TBP in $n$-hexane has been studied. Based on the results of this study, the following conclusions are made.

1. The higher the initial concentration of acetic acid in aqueous solution, the higher the distribution ratio for a fixed TBP concentration and extraction temperature.
2. For a fixed initial concentration of acetic acid in aqueous solution and extraction temperature, the distribution ratio of acetic acid is increased by increasing TBP concentration.
3. The overall equilibrium constants ($K_{pq}$) for the experiments using TBP concentration ranging from 0.05 to 1.00 gmol/dm$^3$ at the extraction temperature of 293 K are found to be 0.1779 to 0.9650.
4. $K_{pq}$ for the experiments at the temperature ranging from 283 to 313 K at the initial concentration of acetic acid of 0.2 gmol/dm$^3$ are found to be 0.1311 to 0.9912.
5. The values of $\Delta H$ and $\Delta S$ are found to be -41.40 kJ/mol and -147.99 J/(mol·K), respectively. The $K_{pq}$ as a function of temperature ($T$) in K can be expressed as $\ln K_{pq} = 5.629/T - 19.92$ with sum of squared error of 0.21.

NOMENCLATURE

$D$ = distribution ratio of acetic acid by TBP (- )

$D_0$ = distribution ratio of acetic acid by pure $n$-hexane (- )

$\Delta H$ = apparent enthalpy change (kJ/mol)

$K_2$ = dimerization constant of acetic acid in the organic phase (dm$^3$/mol)
\[ K_a = \text{dissociation constant of acetic acid in the aqueous phase (mol/dm}^3) \]
\[ K_d = \text{distribution constant of the monomeric acid defined in Eq. (1) ( - )} \]
\[ K_{pq} = \text{overall equilibrium constant defined in Eq. (12) ((mol/dm}^3)^{1-p-q}) \]
\[ p = \text{number of acetic acid molecules involved in the complex} \]
\[ q = \text{number of TBP molecules involved in the complex} \]
\[ R = \text{universal gas constant (8.314 J/(mol·K))} \]
\[ \Delta S = \text{apparent entropy change (J/(mol·K))} \]
\[ T = \text{temperature (K)} \]
\[ [ ] = \text{molar concentration of species in the brackets (mol/dm}^3) \]

Subscripts
\[ t = \text{total value at equilibrium} \]
\[ 0 = \text{initial} \]

REFERENCES


BRIEF BIOGRAPHY OF PRESENTER

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