Equilibrium Study on Reactive Extraction of Lactic Acid with Tri-*n*-Butyl Phosphate in *n*-Hexane

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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. In the extraction process, selection of the solvent is an important aspect to be considered. Considering its solubility in water, cost and availability, tri-*n*-butyl phosphate (TBP) seems to be an attractive solvent for the extraction of lactic acid from aqueous solution.

The purpose of this experiment is to study the equilibrium of the reactive extraction of lactic acid in aqueous solution with TBP in *n*-hexane. The parameters studied in this experiment were initial concentration of lactic acid in the aqueous phase, TBP concentration in *n*-hexane phase, and the extraction temperature. The experiments at ambient temperature were carried out using a separatory funnel, while the experiments at other than ambient temperature were carried out using erlenmeyer flask and water bath shaker to adjust the temperature. In this experiment, the initial concentration of lactic 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 experimental results showed that the higher the initial concentration of lactic acid in aqueous solution, the higher the distribution ratio for a fixed TBP concentration and extraction temperature. For a fixed initial concentration of lactic acid in aqueous solution and extraction temperature, the distribution ratio of lactic acid is increased by increasing TBP concentration. 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 0.0668 to 0.5144. K_{pq} for the experiments at the temperature ranging from 283 to 313 K at the initial concentration of lactic acid of 0.2 gmol/L are found to be 0.0122 to 0.8856. The K_{pq} as a function of temperature (T) in K can be expressed as ln K_{pq} = 10,596/T - 38.08 with sum of square of error of 0.14.

Keywords: Reactive Extraction, Equilibrium, Lactic 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% (w/w).[1] Separation, purification and even to concentrate the fermentation products are very difficult because affinities between acids and water is very strong. Separation of acids and water by distillation is energy consumable to evaporate water.[1] 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.[2] This method of recovery results low yield of acid crystallization, costly, and unfriendly to the environment.[3, 4]

To recovery carboxylic acids 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. To increase the distribution ratio, reactive extraction is one of the method used to recovery carboxylic acids from dilute solutions.[5] Many researchers have investigated reactive extraction of carboxylic acids using some extractants. Juang and Huang[5] has studied the equilibrium of reactive extraction of lactic acid with an amine extractant. Synergistic extraction of lactic acid with tri-*n*-octylamine and TBP has been studied by Matsumoto *et al*.[6]

This paper presents the equilibrium of reactive extraction of lactic acid with TBP in *n*-hexane. TBP reacts with lactic acid to form complexes, while *n*-hexane functions to dilute TBP. TBP has an advantage as solvent for use in aqueous extraction due to its negligible solubility in water.[7]

Experimental

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

Experimental Procedure
The experiments were done for the extraction of lactic acid with pure *n*-hexane and for the extraction of lactic acid with TBP diluted by *n*-hexane. For measuring the distribution ratio of lactic acid in *n*-hexane, the aqueous solution of lactic acid with a fixed concentration and *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, lactic acid concentration in the aqueous phase was determined by titration with known concentration of NaOH solution using phenolphthalein as indicator. The concentration of lactic acid in organic phase was calculated by total mass balance of lactic acid. The experimental parameters were temperature (283, 293, 303, and 313 K) and lactic acid initial concentration (0.1, 0.2, 0.3, 0.5, and 0.5 mol/dm^3).

The experiments for the extraction of lactic acid with TBP in *n*-hexane were carried out by shaken of equal volume (50 cm^3) of aqueous solution of lactic acid with solution of TBP in *n*-hexane. The experimental procedure was similar to that explained above, with the experimental parameters of temperature (283, 303, and 313 K), lactic acid initial concentration (0.1, 0.2, 0.3, 0.5, and 0.5 mol/dm^3), and TBP concentrations (0.1, 0.2, 0.5, and 1.0 mol/dm^3).

Mathematical Modeling

Extraction of Lactic Acid with Pure *n*-Hexane
Most carboxylic acids such as lactic acid mainly exist as dimers in organic phase due to the strong intermolecular hydrogen-bonding, especially in the non-polar or lowly polar solvents.[5] 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.[3, 5]

The reactions in this extraction as the aqueous pH is far less than the dissociation constant of lactic acid (pK_a =3.86) are as follows:[5]

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

$$\text{HA} \Leftrightarrow \overline{\text{HA}}; \quad K_d = \frac{\left|\overline{HA}\right|}{[HA]} \tag{1}$$

Dimerization of lactic acid in the organic phase.

$$2\overline{\text{HA}} \Leftrightarrow \overline{(\text{HA})_2}; \quad K_2 = \frac{\left[\overline{(HA)_2}\right]}{\left[\overline{HA}\right]^2} \tag{2}$$

Dissociation of lactic acid in aqueous phase.

$$\text{HA} \Leftrightarrow \text{H}^+ + \text{A}^-; \quad K_a = \frac{\left[H^+\right]\left[A^-\right]}{[HA]} \tag{3}$$

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

$$\left[\overline{HA}\right]_t = \left[\overline{HA}\right] + 2\left[\overline{(HA)_2}\right] \tag{4}$$

$$[HA]_t = [HA] + \left[A^-\right] \tag{5}$$

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

$$D_0 = \frac{\left[\overline{HA}\right]_t}{[HA]_t} \tag{6}$$

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

The concentration of lactic acid in aqueous phase at equilibrium is determined by titration using NaOH solution with phenolphthalein as indicator, while its concentration in the organic phase is calculated by mass balance as follows:

$$[HA]_t V_0 = \left[\overline{HA}\right]_t V_{org} + [HA]_t V_1 \tag{7}$$

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

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

$$= \frac{\dfrac{\left[\overline{HA}\right]}{[HA]} + \dfrac{2\left[\overline{(HA)_2}\right]}{[HA]}\dfrac{\left[\overline{HA}\right]^2}{\left[\overline{HA}\right]^2}\dfrac{[HA]}{[HA]}}{\dfrac{[HA]}{[HA]} + \dfrac{\left[A^-\right]}{[HA]}\dfrac{\left[H^+\right]}{\left[H^+\right]}} \tag{8}$$

or $D_0 = \dfrac{K_d + 2K_d^{\,2}K_2[HA]}{1 + \dfrac{K_a}{\left[H^+\right]}}$ \hfill (9)

The value of $[HA]$ at Eq. (9) can be obtained from Eq. (5) and at the measured equilibrium pH, that is $\left[A^-\right] = \left[H^+\right]$, so that:

$$[HA] = [HA]_t - \left[H^+\right] \tag{10}$$

Eq. (9) can be arranged as:

$$D_0\left(1 + \frac{K_a}{\left[H^+\right]}\right) = K_d + 2K_d^{\,2}K_2[HA] \tag{11}$$

By plotting $D_0\left(1 + \dfrac{K_a}{\left[H^+\right]}\right)$ versus $[HA]$, we get the value of K_d as the intercept of the graph and $2K_d^{\,2}K_2$ as its slope. The values of K_d and K_2 can also be obtained by linear regression method.

Extraction of Lactic Acid with TBP

The extraction of lactic acid with TBP in *n*-hexane at pH far less than pK_a can be expressed by the following stoichiometry:[5]

$$pHA + q\overline{TBP} \Leftrightarrow \overline{(HA)_p(TBP)_q} \; ; \; K_{pq} \tag{12}$$

where K_{pq} is the extraction equilibrium constant, which is given by Eq. (13).

$$K_{pq} = \frac{\left[\overline{(HA)_p(TBP)_q}\right]}{[HA]^p\left[\overline{TBP}\right]^q} \tag{13}$$

The total concentration of lactic acid in the organic phase can be expressed by Eq. (14) or Eq. (15) as follows:

$$\left[\overline{HA}\right]_t = \left[\overline{HA}\right] + 2\left[\overline{(HA)_2}\right] + \sum_p\sum_q p\left[\overline{(HA)_p(TBP)_q}\right] \tag{14}$$

$$\left[\overline{HA}\right]_t = K_d[HA] + 2K_2K_d^2[HA]^2 + \sum_p\sum_q p\left[\overline{(HA)_p(TBP)_q}\right] \tag{15}$$

Eq. (15) shows that the amount of lactic acid complexed with TBP is corrected by subtracting that physically extracted by pure *n*-hexane from the measured $\left[\overline{HA}\right]_t$. The values of K_d and K_2 in Eq. (15) are calculated from the experimental data of the extraction of lactic acid using pure *n*-hexane. The value of $[HA]$ is calculated by Eq. (10) and the value of $\left[\overline{HA}\right]_t$ is calculated from the total mass balance. So the value of $\left[\overline{(HA)_p(TBP)_q}\right]$ can be calculated as follows:

$$\left[\overline{(HA)_p(TBP)_q}\right] = \frac{1}{p}\left[\left[\overline{HA}\right]_t - K_d[HA] - 2K_2K_d^2[HA]^2\right] \tag{16}$$

The value of $\left[\overline{TBP}\right]$ in Eq. (13) is obtained from the TBP mass balance as expressed by Eq. (17).

$$\left[\overline{TBP}\right] = \left[\overline{TBP}\right]_O - \sum_p\sum_q q\left[\overline{(HA)_p(TBP)_q}\right] \tag{17}$$

Knowing the values of $\left[\overline{(HA)_p(TBP)_q}\right]$, $[HA]$, and $\left[\overline{TBP}\right]$, then the value of K_{pq} in Eq. (13) can be obtained. In this calculation, both number of lactic acid molecules involved in the complex (p) and number of TBP molecules involved in the complex (q) are assumed to be 1.

The complexation reaction between lactic 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 (ΔS). Therefore, as the temperature (T) is increased, the amount of lactic acid extracted decreases. If the enthalpy (ΔH) and entropy of reaction are assumed to be constant over the temperature range, the following expression:

$$\ln K_{pq} = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \tag{18}$$

indicates that a plot of ln K_{pq} vs *1/T* gives a straight line.[1] 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 lactic acid with pure *n*-hexane as a function of initial lactic 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 lactic 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 lactic acid in the aqueous solution.
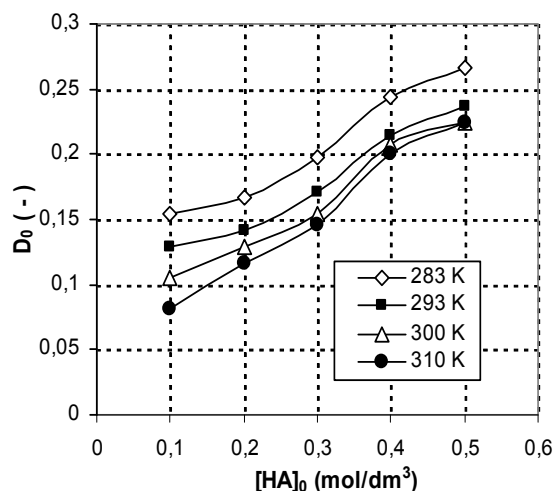

Figure 1. Effects of initial lactic acid concentration and temperature on the distribution ratio of the extraction of lactic acid with pure *n*-hexane.

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. (11). The values of K_a, K_2, and K_d as a function of temperature are shown in **Figure 2**. **Figure 2** depicts that K_a increases as a function of the temperature. K_a attains the maximum value of 33.3 x 10^{-5} mol/dm^3 at 300 K, then decreases to the value of 17.8 x 10^{-5} mol/dm^3 at 310 K. The value of K_2 increases as a function of temperature, while the value of K_d is decreased by increasing the temperature.
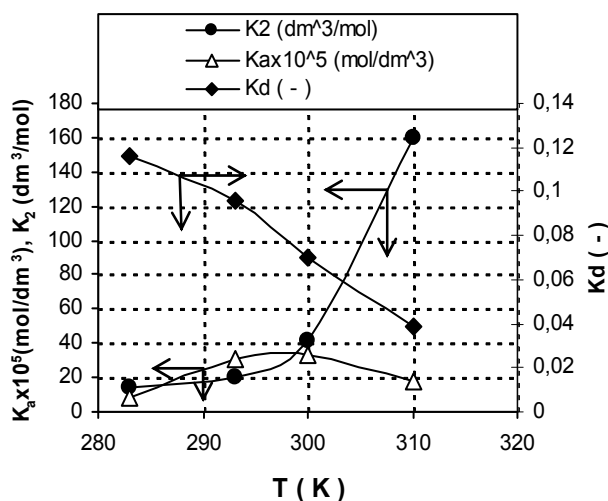

Figure 2. Values of K_a, K_2, and K_d as a function of temperature.

Figure 3 illustrates the distribution ratio of the extraction of lactic acid with TBP in *n*-hexane as a function of initial lactic 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 lactic 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.
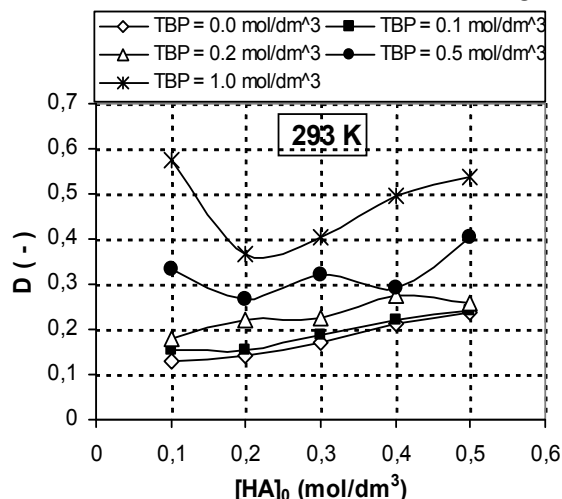

Figure 3. Effects of initial lactic acid and TBP concentrations on the distribution ratio of the extraction of lactic acid with TBP in *n*-hexane at 293 K.

The effect of temperature on the distribution ratio of extraction of lactic acid with TBP in *n*-hexane is shown in **Figure 4**. The complexation reaction of lactic 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 lactic acid extracted decreases.[1, 5]
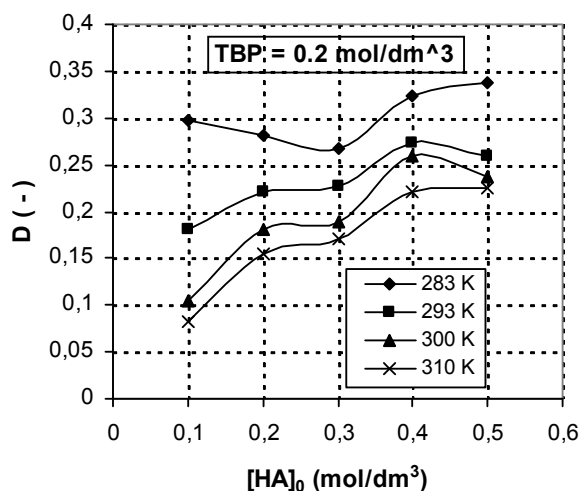

Figure 4. Effect of temperature on the distribution ratio of extraction of lactic acid with TBP in *n*-hexane at the TBP concentration of 0.2 mol/dm^3.

Figure 5 reveals the temperature dependence of the equilibrium constant K_{pq}. It can be seen at **Figure 5** that the extraction of lactic acid with TBP is exothermic. The enthalpy of reaction (ΔH) is obtained from the slope of the graph and it was found to be -88,1 kJ/mol, and the intercept is proportional to the entropy (ΔS) and it was found to be -316.6 J/(mol·K).
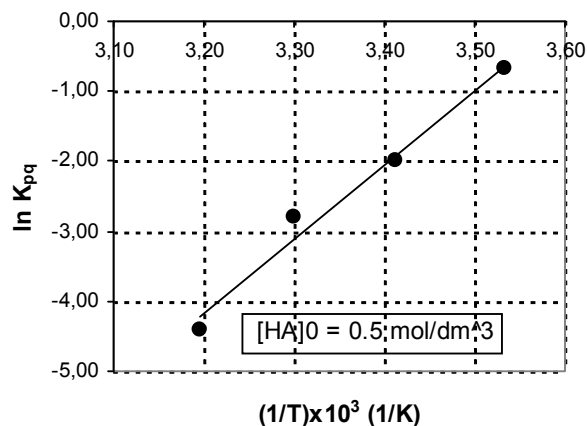
Figure 5. Temperature dependence of the equilibrium constant K_{pq}.

Conclusions

The reactive extraction of lactic 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 lactic acid in aqueous solution, the higher the distribution ratio for a fixed TBP concentration and extraction temperature.
2. For a fixed initial concentration of lactic acid in aqueous solution and extraction temperature, the distribution ratio of lactic acid is increased by increasing TBP concentration.
3. 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 found to be 0.0668 to 0.5144.
4. K_{pq} for the experiments at the temperature ranging from 283 to 313 K at the initial concentration of lactic acid of 0.2 gmol/dm^3 are found to be 0.0122 to 0.8856.
5. The values of ΔH and ΔS are found to be -88,1 kJ/mol and -316.6 J/(mol·K), respectively. The K_{pq} as a function of temperature (T) in K can be expressed as ln K_{pq} = 10,596/T - 38.08 with sum of square of error of 0.14.

Nomenclature

D = distribution ratio of lactic acid by TBP (dimensionless)
D_0 = distribution ratio of lactic acid by pure *n*-hexane (dimensionless)
ΔH = apparent enthalpy change (kJ/mol)
K_2 = dimerization constant of lactic acid in the organic phase (dm^3/mol)
K_a = dissociation constant of lactic acid in the aqueous phase (mol/dm^3)
K_d = distribution constant of the monomeric acid defined in Eq. (3) (dimensionless)
K_{pq} = overall equilibrium constant defined in Eq. (13) ((mol/dm^3)$^{1-p-q}$)
p = number of lactic acid molecules involved in the complex
q = number of TBP molecules involved in the complex
R = universal gas constant (8.314 J/(mol·K))
ΔS = apparent entropy change (J/(mol·K))
T = temperature (K)
[ ]   = molar concentration of species in the brackets (mol/dm^3)

Subscripts

l   = liquid phase
org = organic phase
t   = total value at equilibrium
0   = initial

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