

Effect of pH on the Extraction Characteristics of Succinic and Formic Acids with Tri-n-octylamine Dissolved in 1-Octanol

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Abstract A study was made on the extraction equilibria of succinic and formic acids from aqueous solutions using tri-n-octylamine (TOA) in 1-octanol. It was shown that the loading values of TOA decreased with increasing pH values. The apparent equilibrium constants for each acid-amine complex were determined by an equilibrium model. In the case of succinic acid, the formation of a bisuccinate anion played an important role in the stoichiometry of the acid-amine complex.

Keywords: succinic acid, formic acid, pH values, loading

INTRODUCTION

Succinic acid is a dicarboxylic acid that is produced as an intermediate in the tricarboxylic acid cycle (TCA) and also as one of the fermentation products of anaerobic metabolism. Fermentation-derived succinic acid has the potential to become a large-volume industrial chemical that could form the basis for supplying many intermediate and specialty chemicals for the consumer product industry [1]. Lee et al. (1999) reported that the maximum yield was 0.99 g succinic acid/g of glucose consumed in the fermentation process by *Anaerobiospirillum succiniproducens* [2]. Recently, Lee isolated *Mannheimia* sp. 55E from bovine rumens. In the anaerobic fermentation that was used for the production of succinic acid, the compositions of the fermentation broth were 13 g/L succinic acid and 4 g/L formic acid [3].

However, succinic acid is relatively nonvolatile, therefore distillation is not a useful recovery process. At present, the prevailing recovery process involves the precipitation of the calcium salt of the acids. The classical product recovery method is based on the precipitation of the calcium salt after the addition of calcium hydroxide to the aqueous fermentation broth. The precipitation method also has disadvantages such as the substantial cost of chemicals, a low yield in crystallization and product loss [4].

A reactive extraction method has been proposed to be as an effective primary separation step for the recovery of carboxylic acids from a dilute fermentation broth. This separation process is based on the reaction between

extractant and carboxylic acid [5-7]. The extractant in the organic phase reacts with carboxylic acid in the aqueous phase and then the reaction complex that is formed is solubilized into the organic phase.

There are three categories of extractants that are used in reactive extraction. These are the carboxylic acid extraction by solvation with carbon-bonded oxygen-bearing extractants, by solvation with phosphorous-bonded oxygen-bearing extractants, and by proton transfer or by ion-pair formation using high molecular weight aliphatic amines [8]. It has been reported that the aliphatic amine extractants are more effective than other extractants. Among the aliphatic amines, tertiary amines are the most widely used for the recovery of carboxylic acids because the primary and the secondary amines tend to react irreversibly with carboxylic acid and stripping the solvent becomes difficult [9]. In general, tertiary amines extract only the undissociated form of the carboxylic acid. In contrast, quaternary amines can extract both the undissociated and dissociated acids. However, the regeneration process is difficult.

There are several factors that influence the extraction characteristics of carboxylic acid such as pH, concentration of carboxylic acid and amine, polarity of the diluent and the operating temperature. Among these factors, pH is considered to be the important factor in the amine-based extraction process since the equilibrium in amine-based extraction is dependent upon the degree of dissociation of carboxylic acid in an aqueous phase.

In the present study, the extraction equilibria of succinic and formic acids with tri-n-octylamine (TOA) in 1-octanol were investigated. The formulation of the acid-amine complexes for each carboxylic acid was numerically determined by the least-square method. Finally, extraction characteristics of aqueous solutions containing succinic acid and formic acid were studied.

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EQUILIBRIUM MODEL OF THE CARBOXYLIC ACID-TOA COMPLEXES

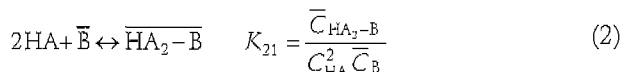
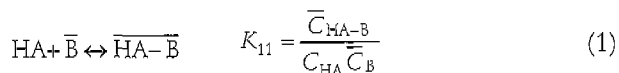
In the amine-based extraction of carboxylic acid, the reaction between carboxylic acid and amine can be described in various ways. Equilibrium data of amine-based extraction can be explained by the mass action law based on these reactions.

Some assumptions in the present description are required as follows:

(1) The solubility of TOA in the aqueous phase is negligible.

(2) TOA reacts only with the undissociated form of acid.

It is well known that carboxylic acids may exist as dimers in the organic phase because of the intermolecular hydrogen bonding [10]. Based on these assumptions, the reactions of monocarboxylic acid by TOA can be described as follows:



The relationship between the pH value and the pK_A value is represented as follows:

$$\text{pH} = \text{pK}_A + \log \frac{C_{\text{A}^-}}{C_{\text{HA}}} \quad (3)$$

From Equ. (3), the concentration of undissociated monocarboxylic acid is given by

$$C_{\text{HA}} = \frac{C_{\text{HA},\text{total}}}{1 + 10^{\text{pH} - \text{pK}_A}} \quad (4)$$

The total equilibrium concentration of monocarboxylic acid in the organic phase is obtained as follows:

$$\bar{C}_{\text{HA}} = \bar{C}_{\text{HA}-\text{B}} + 2\bar{C}_{(\text{HA})_2-\text{B}} = K_{11} C_{\text{HA}} \bar{C}_{\text{B}} + 2K_{21} C_{\text{HA}}^2 \bar{C}_{\text{B}} \quad (5)$$

The concentration of free (unreacted) TOA is

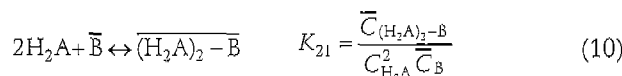
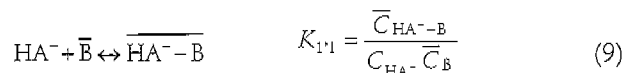
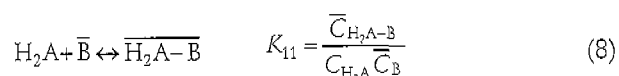
$$\bar{C}_{\text{B}} = C_{\text{B}}^0 - \bar{C}_{\text{HA}-\text{B}} - 2\bar{C}_{(\text{HA})_2-\text{B}} = C_{\text{B}}^0 - K_{11} C_{\text{HA}} \bar{C}_{\text{B}} - 2K_{21} C_{\text{HA}}^2 \bar{C}_{\text{B}} \quad (6)$$

From Eqs. (5) and (6), the loading of TOA, Z can be written,

$$Z = \frac{\bar{C}_{\text{HA}}}{C_{\text{B}}^0} = \frac{K_{11} C_{\text{HA}} + 2K_{21} C_{\text{HA}}^2}{1 + K_{11} C_{\text{HA}} + K_{21} C_{\text{HA}}^2} \quad (7)$$

Here, the concentration of the undissociated acid in the aqueous phase can be obtained from Equ. (4) and the measured pH values.

For a dicarboxylic acid such as succinic acid, the reaction of undissociated acid and bicarboxylate anion with TOA must be considered as follows:



Although succinic acid is a dicarboxylic acid, it is difficult for the (1,2) acid-amine complex to be formed.

The concentrations of undissociated acid and bicarboxylic anion are expressed as follows:

$$C_{\text{H}_2\text{A}} = \frac{C_{\text{H}_2\text{A},\text{total}}}{1 + 10^{\text{pH} - \text{pK}_{A1}} + 10^{2\text{pH} - \text{pK}_{A1} - \text{pK}_{A2}}} \quad (11)$$

$$C_{\text{HA}^-} = \frac{C_{\text{H}_2\text{A},\text{total}} \cdot 10^{\text{pH} - \text{pK}_{A1}}}{1 + 10^{\text{pH} - \text{pK}_{A1}} + 10^{2\text{pH} - \text{pK}_{A1} - \text{pK}_{A2}}} \quad (12)$$

By the same procedure that was used in the case of monocarboxylic acid, the loading value, Z , is given by:

$$Z = \frac{K_{11} C_{\text{H}_2\text{A}} + K_{1'1} C_{\text{HA}^-} + 2K_{21} C_{\text{H}_2\text{A}}^2}{1 + K_{11} C_{\text{H}_2\text{A}} + K_{1'1} C_{\text{HA}^-} + K_{21} C_{\text{H}_2\text{A}}^2} \quad (13)$$

MATERIALS AND METHODS

Materials

Succinic acid (Sigma, 99.9%, $\text{pK}_{A1}=4.207$, $\text{pK}_{A2}=5.635$) and formic acid (Fluka, 98.0%, $\text{pK}_A=3.751$) were used as received from the manufacturer to prepare the carboxylic acid solutions having various pH values and concentrations.

The initial concentrations of each carboxylic acid were 13.0 g/L (succinic acid) and 4.0 g/L (formic acid) which are based on the composition of the fermentation broth by *Mannheimia* sp.

The pH of the solution was adjusted by adding either a NaOH or HCl solution. The solution pH was measured using a Corning digital ion analyzer 255 that was equipped with an Orion Ross combination pH electrode.

Tri-*n*-octylamine (TOA) (Aldrich) was used as received from the manufacturer. The diluent mainly used in this study was 1-octanol (Aldrich) which is a polar, water-insoluble alcohol.

Experimental Procedures

Equal volumes (10 mL) of an organic solvent that contained the amine and diluent and an aqueous solution of carboxylic acid were placed in 30 mL vials. These were put in a water bath in order that was stirred by magnetic bar in water bath at 1,000 rpm and 25°C for 2 h, followed by centrifuging at 4,000 rpm for about 15 min in order to separate the two phases.

The concentrations of the organic acid were measured by HPLC with an ion exchange column (Supercogel C-601H, 300 mm × 7.8 mm, SUPELCO, USA) using 0.1 wt% H_3PO_4 as the mobile phase.

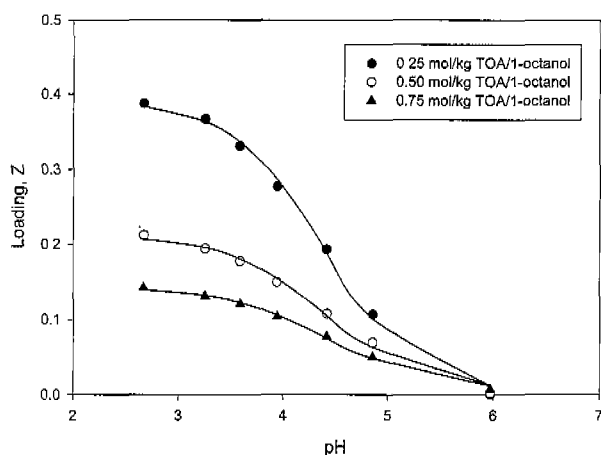


Fig. 1. Loading-pH isotherm in the reactive extraction of succinic acid (Initial concentration of succinic acid was 13 g/L).

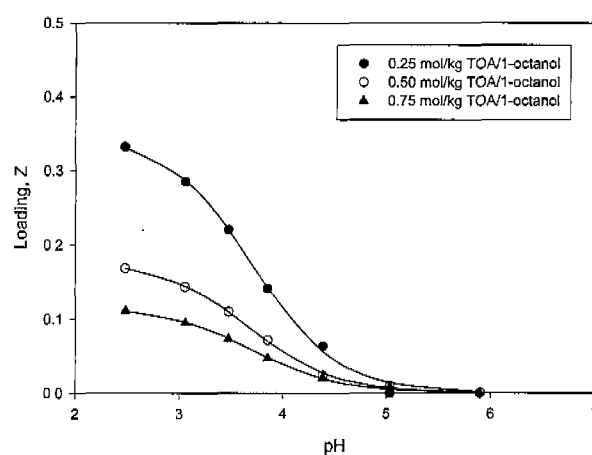


Fig. 2. Loading-pH isotherm in the reactive extraction of formic acid (Initial concentration of formic acid was 4 g/L).

RESULTS AND DISCUSSION

Effect of pH

Aliphatic amines extract carboxylic acids from an aqueous phase by forming an acid-amine complex with the undissociated acid. Because the concentration of the undissociated acid is a function of pH values as seen in Eqs. (4), (11), and (12), the extraction of carboxylic acids is seen to be influenced with pH value in the aqueous phase.

Fig. 1 shows the effect of pH on the loading values for succinic acid. For all amine concentrations, the loading values decreased as the values of pH increased. A decrease in the values of the pH means that the concentration of undissociated acid increased. In general, the loading value increases with decreasing values of pH except at extremely high or low pHs, where the loading values do not change significantly [11]. In particular, there are asymptotic points in each curve near the pK_{A1} value of the succinic acid. We conclude that the extractability can be influenced by the concentration of undissociated acid. The concentration of bicarboxylate anion, which exists above the pK_{A2} , has little influence on the extractability.

The effect of pH values on the extractability of the formic acid is shown in Fig. 2. The results of the formic acid were similar to those of the succinic acid; *i.e.*, the loading values decreased with an increasing pH and a decreasing concentration of TOA. The sharp decreasing in the loading values for formic acid with increasing pH began at lower values of pH than those that were found for succinic acid. This result can be attributed to the lower pK_A value for formic acid relative to that of succinic acid. In spite of a low concentration of formic acid (4 g/L) the loading value for formic acid was almost that of succinic acid in an acidic pH. Generally, the more acidic the acid, as measured by the pK_A , the more it can be extracted, given the same solvent system [12].

The apparent equilibrium constants of the reactive

Table 1. Apparent equilibrium constants in the reactive extraction of each acid by pH

	TOA concentration [mol/kg]	K_{11} [mol ⁻¹ kg]	$K_{1,1}$ [mol ⁻¹ kg]	$K_{2,1}$ [mol ⁻² kg ²]
Succinic acid	0.25	5.09	0.26	2.57
	0.50	2.30	0.34	0.52
	0.75	1.50	0.31	0
Formic acid	0.25	3.18	-	13.66
	0.50	1.56	-	4.98
	0.75	1.14	-	2.12

extraction for succinic and formic acids as a function of pH are given in Table 1. As seen in Table 1, the ratio of the apparent equilibrium constant for (2,1) to those for (1,1) complexes for succinic acid is small compared with the same ratio for formic acid. This behavior can be attributed in large measure to the fact that the acidity of the succinic acid is stronger than that of the formic acid [13]. The $K_{2,1}$ increased with decreasing of TOA concentration. In the case of formic acid, the $K_{2,1}$ values are especially higher than those for succinic acid. We conclude that the dimer formation of formic acid by means of the intermolecular hydrogen bonding is easy. However, in the case of succinic acid, the formation of intermolecular hydrogen bonding is not as easy as in the case of formic acid. This can be explained by the formation of bisuccinate anion by intramolecular hydrogen bonding. Because succinic acid is a dicarboxylic acid, the intramolecular hydrogen bonding between the two carboxylic groups by means of a rotation of the central C-C bond is possible. In 0.75 mol/kg TOA dissolved in 1-octanol, the $K_{2,1}$ is near 0. Therefore, the amount of dimer formation of succinic acid decreased as the TOA concentration increased because of the high extractability of TOA.

Reactive Extraction in Aqueous Solution Containing Succinic and Formic Acid

The initial concentrations of succinic and formic acid

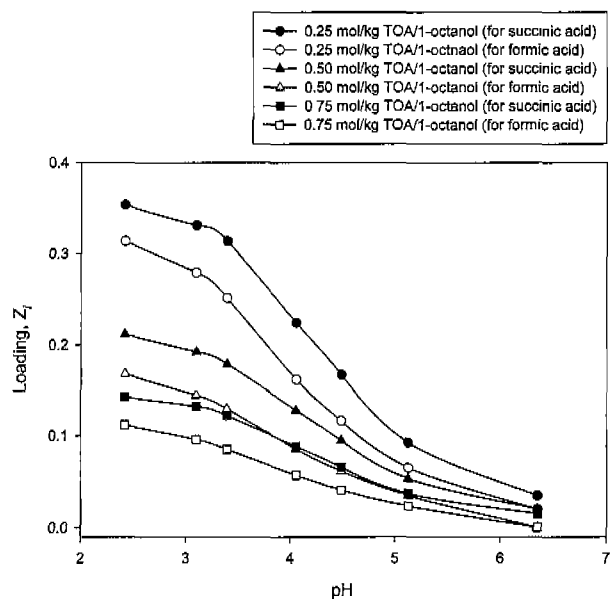


Fig. 3. Loading-pH isotherm in the reactive extraction of aqueous mixtures that contained succinic and formic acids (The initial concentrations of succinic and formic acids were 13 g/L and 4 g/L, respectively.).

were 13 g/L and 4 g/L, respectively.

Fig. 3 shows the experimental loading values according to pH in the reactive extraction of succinic and formic acid into TOA from an aqueous acid mixture. As the value of pH decreases, the concentration of dissociated acid increases. We found that succinic acid is preferentially extracted from the mixture because it is the weaker acid, based on pK_A values.

In the quantification of the degree of selectivity between the acids, the separation factor for succinic acid is defined as follows:

$$\alpha_{SA/FA} = \frac{(C_{SA}^{org} / C_{FA}^{org})}{(C_{SA}^{raf} / C_{FA}^{raf})} = \frac{C_{SA}^{org} C_{FA}^{raf}}{C_{SA}^{raf} C_{FA}^{org}} = \frac{D_{SA}}{D_{FA}} \quad (14)$$

where $C_{aq,i}$ and $C_{org,i}$ are the equilibrium concentrations of the i components in aqueous phase and organic phases, respectively. Fig. 4 shows the separation factor-pH isotherms for succinic acid and formic acid. The separation factor rises to a maximum at $pH \approx 3.3$ for the 0.25 and 0.50 mol/kg TOA dissolved in 1-octanol. This maximum peak might be attributed to the pK_A value of formic acid (pK_A value of formic acid = 3.751). Below the maximum point, formic acid was preferentially extracted. However, all the succinic and formic acid was dissociated above the pK_{A1} value of the succinic acid, therefore the selectivity for the specific acid did not occur. In 0.75 mol/kg TOA dissolved in 1-octanol, the maximum point shifted to $pH \approx 4.5$. This was because the extractability of TOA is proportional to its concentration in 1-octanol.

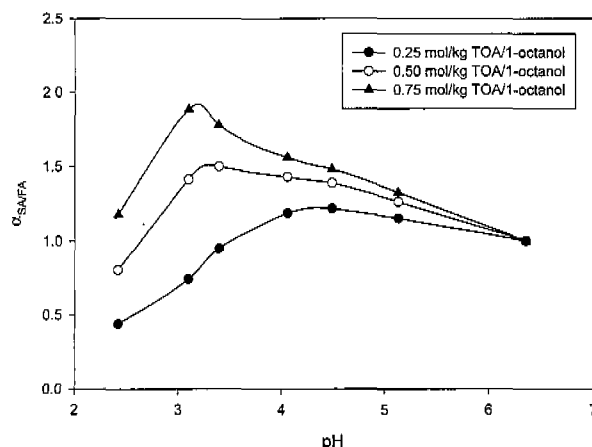


Fig. 4. Effect of pH on the separation factors for succinic acid in the reactive extraction of aqueous mixtures that contained succinic and formic acids (Initial concentrations of succinic and formic acids were 13 g/L and 4 g/L, respectively.).

CONCLUSION

The effect of pH values on the extraction equilibria of succinic and formic acids in aqueous solutions by TOA in 1-octanol have examined and compared. The loading values decreased with increasing pH values and a sharp decrease in TOA loading as a function of increasing pHs began at different pH according to the pK_A values of each acid. An equilibrium model based on several assumptions showed good agreement with the obtained experimental results.

The reactive extraction of aqueous solution containing succinic acid and formic acid was carried out.

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