

Reactive Extraction of Carboxylic Acids (Butyric-, Lactic-, Tartaric-, Itaconic- Succinic- and Citric Acids) using Tri-n-Butylphosphate (TBP) Dissolved in 1-Dodecanol and n-Octane (1:1 v/v)

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Abstract:

In the last 3-4 decades, the production of fermentation chemicals has an increased interest, as petrochemical prices have been increasing. Hence there is an essential need to intensify the fermentation technology to make more economically viable as conventional separation processes are expensive for recovery of fermentation chemicals. Liquid-liquid extraction with an efficient extractant and diluent system has been proposed as an alternative to the classical precipitation (conventional separation) process and there have been several recent efforts to develop process technologies based on reactive extraction. In the present study, the reactive extraction of six different carboxylic acids such as tartaric acid, succinic acid, itaconic acid, citric acid, lactic acid and butyric acid are carried out. 15% of tri-n-butylphosphate (TBP) in a mixture of 1-dodecanol (active diluent or modifier) and n-octane (1:1 v/v) is used as an extractant/diluent system. The extraction efficiency is calculated in terms of distribution coefficient (K_D) and degree of extraction (E). Based on the equilibrium experimental data and law of mass action for chemical equilibrium (Chemodel), equilibrium parameters (the values of equilibrium constant and type of complex formed) are determined. The orders of extraction for these acids are determined based on their extractability and found to be in the order of butyric acid > itaconic acid > succinic acid > lactic acid > citric acid > tartaric acid. These data will be useful for the intensification of separation of carboxylic acids from fermentation broth using reactive extraction.

Keywords: Carboxylic Acids; Reactive Extraction; Equilibrium; Extractant (TBP); Chemodel.

INTRODUCTION

Carboxylic acids are small organic acids with one or more carboxylic acid groups. Their properties vary significantly with their carbon-chain length, molecular structure, and the presence of additional functional groups. Figure 1 shows some important carboxylic acids and their chemical structures. These carboxylic acids are currently produced either from petroleum-based feedstocks through chemical synthesis or from carbohydrates via fermentation. Originally, all industrial carboxylic acids were produced by biochemical processes. By the mid-twentieth century, petrochemical processes had begun to replace biochemical routes, and they are now the primary industrial methods for manufacturing many carboxylic acids, including acetic, propionic, butyric, fumaric, malic, and acrylic acids [1].

However, several carboxylic acids, such as citric, gluconic, and itaconic acids, continue to be produced, solely by fermentation, largely because their complex chemical structures are difficult to produce via chemical synthesis. Citric, fumaric, malic, succinic, and itaconic acids are multifunctional carboxylic acids. Their current industrial applications include uses as food acidulents and in the manufacture of polyester resins. They can also be used as building blocks for the synthesis of esters and biodegradable polymers. Commercially, maleic anhydride is the precursor for the production of fumaric (*trans*-butenedioic acid), malic (hydroxyl succinic acid), and succinic acids. With the increasing oil price, concerns about oil supplies and environmental pollution caused by petrochemical processes, and consumer demand for natural food ingredients, there has been a high level of interest in producing carboxylic acids from renewable resources using bioprocesses. The production of industrially important carboxylic acids from cheap and abundant recycled biomaterials can reduce wastes and our dependency on imported oils [1].

However, the commercialization has not been done and the reason being the high cost of recovery and the difficult separation of the acid. The traditional recovery process of carboxylic acids from fermentation broth is quite complicated. Conventionally, acid can be recovered by precipitating as calcium salt with calcium hydroxide. In this recovery scheme, calcium salt is precipitated, recovered by filtration and converted to acid by addition of sulphuric acid. In the present work, the reactive extraction of carboxylic acids produced via fermentation, which is an intensified version of liquid-liquid extraction is studied [2-3].

Organophosphorus compounds and long-chain aliphatic amines are effective extractants for the separation of carboxylic acids from dilute aqueous solution [2,3]. Phosphorus-bonded, oxygen-containing extractants have a phosphoryl group and a stronger Lewis basicity than those of carbon-bonded, oxygen-containing extractants. Phosphorus-bonded, oxygen-containing extractants can only co-extract small amounts of water, and show low solubilities in water. When organophosphorus extractants are used, the solvation has a higher specificity. Generally, organophosphorus-based and amine-based extractants are dissolved in a diluent such as a ketone, an alcohol, hydrocarbons, etc. to provide appropriate physical properties for use in the extraction

process. Since the presence of hydroxyl and carboxylic groups increases the solubility of acids in the water phase, the strong interactions of solvent with solutes are necessary to extract carboxylic acids from dilute aqueous solutions. Polar diluents that enhance the extraction power of amines are more favorable than nonpolar diluents [4,5]. Such solvating extractants open new avenues in process development and reduce energy and reagent consumption. Extraction of organic acids has been studied using tri-*n*-butyl phosphate [6-10].

In this equilibrium study, a biocompatible mixture of inert (*n*-octane) and active (1-dodecanol) diluents are used to provide the appropriate physical properties of extractant (TBP) and improved extraction efficiency. 1-Dodecanol as modifier is also useful if a third phase is formed during the extraction because of low solubility of acid–extractant complex in the inert diluent. Equilibrium extraction constant (K_E) are determined with mathematical model using experimental data. The results of equilibrium experimental study are useful to design extraction processes for recovery of carboxylic acids from the fermentation broths.

EXPERIMENTAL

Chemicals

Tri-*n*-butyl phosphate, used as extractant, and 1-dodecanol and *n*-octane used as diluents are delivered by Spectrochem Pvt. Ltd., India. All compounds are used without any pretreatment. Aqueous solutions of carboxylic acids such as tartaric acid, succinic acid, itaconic acid, citric acid, lactic acid and butyric acid procured from Sd Fine, India are prepared using distilled water.

Methods

Carboxylic acids are dissolved in distilled water to prepare the aqueous solutions with initial concentration of acid in the range of 0.10 to 0.835 mol·L⁻¹. The organic solutions are prepared by dissolving TBP in 1- dodecanol and *n*-octane at the concentration of 0.55 mol·L⁻¹. Equal volumes of the aqueous and organic solution (16 mL of each phase) are taken in conical flasks of 100 mL and shaken at 100 rpm for 8 hours on a temperature controlled reciprocal shaker bath (HS 250 basic REMI labs) at constant temperature (298K). After attaining equilibrium, both the phases are separated in 125 mL separating funnel. After separation, the aqueous phase is analyzed to determine the concentration of acid by titration using fresh 0.05N NaOH solution and phenolphthalein as an indicator. The acid concentration in the organic phase is calculated by mass balance. For selected data points reproducibility is checked and found that the experimental data are reproducible within ± 5 % of accuracy.

RESULTS AND DISCUSSION

The present work deals with the equilibrium reactive extraction of acids from aqueous solution with TBP (extractant) dissolved in 1- dodecanol (active) and *n*-octane (inactive) diluents at 298 K. The equilibrium experimental data of reactive extraction of

six different acids is presented in Table 1.

Table 1. Equilibrium results for the extraction of carboxylic acids using TBP (0.55 mol.L⁻¹) dissolved in n-octane/1-dodecanol (1:1 v/v) at 298 K

S No.	Acid	Initial Acid Conc., (mol.L ⁻¹)	Aq. Phase Conc. (mol.L ⁻¹)	Org. Phase Conc. (mol.L ⁻¹)	Distribution Coefficient, K _D	Degree of Extraction, E
1	Tartaric	0.800	0.785	0.015	0.019	1.875
		0.500	0.480	0.020	0.042	4.000
		0.250	0.245	0.005	0.020	2.000
		0.100	0.100	0.000	0.000	0.000
2	Succinic	0.803	0.733	0.070	0.096	8.723
		0.502	0.448	0.054	0.121	10.779
		0.251	0.223	0.028	0.127	11.277
		0.100	0.090	0.010	0.115	10.280
3	Citric	0.823	0.797	0.027	0.034	3.239
		0.515	0.502	0.013	0.026	2.510
		0.257	0.248	0.009	0.036	3.482
		0.103	0.097	0.006	0.065	6.073
4	Lactic	0.810	0.763	0.048	0.062	5.864
		0.506	0.470	0.036	0.077	7.161
		0.253	0.235	0.018	0.077	7.161
		0.101	0.083	0.009	0.106	9.589
5	Itaconic	0.768	0.638	0.130	0.204	16.938
		0.480	0.378	0.101	0.268	21.129
		0.240	0.185	0.055	0.297	22.867
		0.096	0.075	0.021	0.279	21.824
6	Butyric	0.835	0.148	0.688	4.661	82.335
		0.522	0.090	0.432	4.799	82.755
		0.261	0.045	0.216	4.799	82.755
		0.104	0.018	0.087	4.964	83.234

The important factors associated with the characteristics of acids which affect their extractability are the number of carboxylic groups, their acid strength (pKa), the nature and number of additional functional groups (keto, hydroxo, pyridine, etc.) on the molecules, and the size & hydration of the anion. Even, mono-carboxylic acids are more extractable than di- or polybasic acids with an equal number of carbon atoms due to an increased affinity for the aqueous solution of acids with two or more functional groups. The highest strength of the complex solvation is found for butyric acid with a maximum degree of extraction (E = 83.23) and followed by itaconic acid (E = 22.87) and other acids. Thus the extractability of acids with TBP in the diluent mixture is found in the order of butyric acid > itaconic acid > succinic acid > lactic acid > citric

acid > tartaric acid. This order permits us to predict which acids may be separated from one another by solvent extraction by TBP. This order is only valid when the diluent used is the same. Since most acids show very low extractability with 15% TBP, further study with higher concentrations of TBP is required for better analysis. Such a study would also permit study of trends on varying extractant concentration. Initial concentration of acids also affects the extraction efficiency of the extractant, TBP. The extraction efficiency (in terms of K_D and E) is found to decrease or remain constant with an increase in the concentration acids. For very low extraction of the acids, no exact trends are found for the variation in extraction efficiency with initial acid concentration.

The extraction process is analyzed by means of the degree of extraction and distribution coefficient. The distribution coefficient, K_D , is calculated using Eq. 1.

$$K_D = \frac{\bar{C}_{HA}}{C_{HA}} \quad (1)$$

where, \bar{C}_{HA} is the total concentration of carboxylic acid in organic phase and C_{HA} is the total acid concentration (dissociated and un-dissociated) in aqueous phase at equilibrium.

The degree of extraction is defined as the ratio of acid concentration in the extracted phase to the initial acid concentration in aqueous solution by assuming no change in volume at equilibrium as given by Eq. 2.

$$E = \frac{K_D}{1 + K_D} \times 100 \quad (2)$$

The model is based on the loading ratio for formation of various types of complexes (1:1 and 2:1) between acid and TBP, as an extractant. The extent to which the organic phase (extractant and diluents) may be loaded with acid is expressed by the loading ratio, Z (ratio of total acid concentration in the organic phase to the total extractant concentration) as given by Eq. (3)

$$Z = \frac{\bar{C}_{HA}}{[S]_{in}} \quad (3)$$

The value of Z depends on the extractability of the acid (strength of the acid-base interaction) and its aqueous concentration. The stoichiometry of the overall extraction equilibrium depends on the loading ratio in organic phase (Z). If the organic phase is not highly concentrated by acid, i.e., at very low loading ratios ($Z < 0.5$), 1:1 complex of acid and extractant is formed. A plot of $Z/(1-Z)$ versus $[HA]$ yields a straight line passing through origin with a slope of complexation constant (K_{E1}) as given by Eq. (4.36):

$$\frac{Z}{1-Z} = K_{E1}[HA] \quad (4)$$

For higher loading ratios (at least, $Z > 0.5$):

$$\frac{Z}{2-Z} = K_{E2}[HA]^2 \quad (5)$$

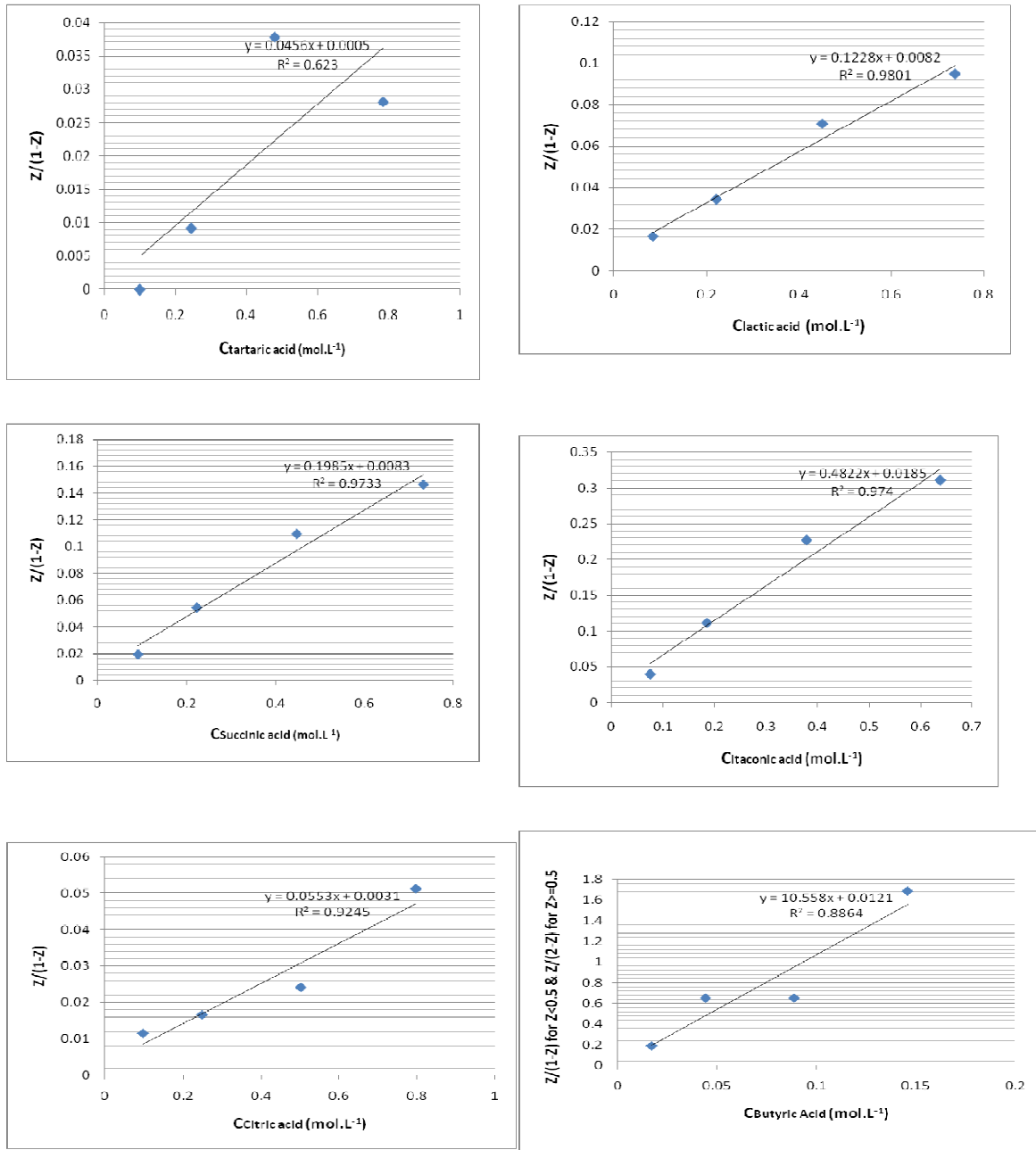


Figure 2. Plot of $Z/(1 - Z)$ versus Aq. phase acids concentration for the estimation of (1:1) acid-TBP equilibrium complexation constant (K_{E1})

Table 2. Equilibrium complexation constant (K_{E1}) for different acids estimated from Figure 2.

Acid	Succinic Acid	Tartaric Acid	Citric Acid	Lactic Acid	Itaconic Acid	Butyric Acid
K_{E1}	0.198	0.045	0.055	0.122	0.482	10.55

The values of equilibrium constants (K_{E1}) for the formation of 1:1 complexes are estimated using Eqs. (3-5) by plotting $Z/(1 - Z)$ vs $[HA]_{aq}$ as shown in Figure 2 for 6 different acids. The values of K_{E1} for 1:1 complex of acid and TBP at 298 K for the extraction of different acids with TBP are given in Table 2. In all the tested acids, butyric acid (mono-carboxylic acid) is the best solvating solute TBP giving ($K_E = 10.6$).

CONCLUSIONS

The studies on reactive extraction of carboxylic acid with TBP dissolved in a mixture of 1-dodecanol (active diluent or modifier) and n-octane (1:1 v/v), at different acid concentrations indicate that the reactive extraction occurs by means of the interfacial formation of solvates between acid and TBP. Different parameters like distribution coefficient, degree of extraction, loading ratio, and equilibrium complexation constants are determined. The extractability of acids with TBP in the diluent mixture is found in the order of butyric acid > itaconic acid > succinic acid > lactic acid > citric acid > tartaric acid. The highest strength of the complex solvation is found for butyric acid with a maximum equilibrium extraction constant ($K_E = 10.6$) and followed by itaconic acid ($K_E = 0.5$).

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