

# Effect of Salts on the Extraction Characteristics of Succinic Acid by Predispersed Solvent Extraction

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**Abstract** Predispersed solvent extraction (PDSE) of succinic acid with Tri-n-octylamine (TOA) dissolved in 1-octanol from aqueous solutions of 50 g/L succinic acid was examined. It was found that the equilibrium data in PDSE was equal to that in conventional solvent extraction in spite of the lack of mechanical mixing in PDSE. The influence of salts on succinic acid extraction and the stability of colloidal liquid aphrons (CLAs) were also investigated. Results indicated that in the presence of sodium chloride, less succinic acid was extracted by CLAs and the stability of CLAs decreased. However, the stability of CLAs was sufficient to make PDSE practically applicable to real fermentation broth, considering the concentration range of salts in the fermentation process for succinic acid.

*Keywords:* PDSE, CLAs, succinic acid, stability

## 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. Uses of succinic acid range from scientific applications such as radiation dosimetry and standard buffer solutions to applications in agriculture, food, medicine, plastics, cosmetics, textiles, and waste-gas scrubbing. Recently, succinic acid has received increasing attention due to its usage as the monomer of polybutylene succinate, a biodegradable polymer [1,2].

Currently, more than 15,000 tons of industrial succinic acid is sold. It is mainly produced by petrochemical processing of maleic anhydride. However, the biological processes for succinic acid such as fermentation and bioconversion are in development stages [3]. The production of succinic acid by fermentation has distinct advantages over petrochemical processing. For example, the succinate fermentation consumes and incorporates carbon dioxide into succinic acid as a carbon dioxide-fixing green technology [4-6].

However, in the production of succinic acid by fermentation, a separation process for succinic acid is needed due to many impurities in the fermentation broth such as acid by-products, carbon sources, and salts. A reactive extraction method has been proposed to be as an effective primary step for separating succinic acid from dilute fer-

mentation broth. This separation process is based on the reaction between extractant and extracted acid. The extractant in the organic phase reacts with acid in the aqueous phase and then the acid-extractant complexes that are formed are solubilized into the organic phase [7]. It has been reported that a tertiary amine is an effective extractant for the separation of succinic acid from its aqueous solution [7,8]. Recently, a blended amine consisting of a short chain and a long chain tertiary amine was developed for the extraction of succinic acid [9].

Conventional solvent extraction requires an energy-consuming mixer-settler and a large volume of extractants. Predispersed solvent extraction (PDSE) using colloidal liquid aphrons (CLAs) can overcome this shortcoming of conventional solvent extraction. CLAs have been defined as a liquid core globule with colloidal dimensions encapsulated by an aqueous soapy shell and dispersed in a continuous aqueous phase. The liquid core contains a small amount of oil soluble surfactant and this size can range from submicron to 50 microns [10]. Sebba proposed the structure of an individual polyaphron [11]. As seen in Fig. 1, an organic solvent is placed inside and the outer surface is made up of a thin aqueous soapy shell. Upon CLA preparation, an aggregate of individual CLAs having a structure resembling that of a biliquid foam is termed a polyaphron. As water is a continuous phase, when a polyaphron is added to water it disperses to give CLAs. This soapy film enables polyaphrons containing extractants to be dispersed in the pregnant phase without any mechanical mixing. In addition, enhancement of mass transfer rates can be achieved due to these micro-sized polyaphrons by increasing the interfacial area.

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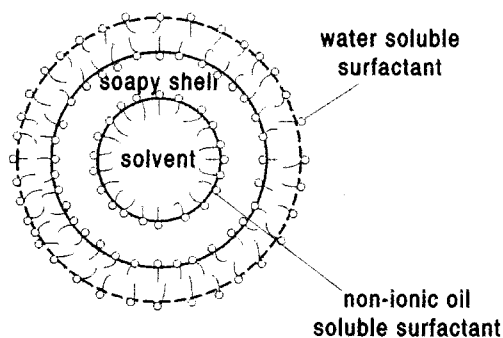


Fig. 1. Structures of CLA.

The schematic structure of CLA is shown in Fig. 1. PDSE using CLAs has been mainly applied to the removal of metal ion from wastewater and the recovery of proteins and carboxylic acids in bioprocessing [12-14].

Generally, a small amount of salts as nutrients was needed in the fermentation production of succinic acid. Salts can influence the performance of fermentation processes but not the extraction characteristics. In the present study, the effect of salt on the extractability of succinic acid and on the stability of CLAs was investigated.

## MATERIALS AND METHODS

### Materials

Succinic acid was obtained from Sigma Chemical Company (St. Louis, MO, USA). It was diluted to 50 g/L in aqueous phase. This concentration was based on the results of anaerobic fermentation by *Anaerobiospirillum succiniciproducens*. Tri-n-octylamine (TOA) (Aldrich) was used as extractant without further purification. The diluent used in this study was 1-octanol (Aldrich), a polar, water-insoluble alcohol. Diluents are essential for these types of experiments due to the highly viscous and corrosive properties of TOA.

### Preparation of CLAs

CLAs were prepared by the following method. A stable-foam was obtained by mixing of an aqueous phase containing 4 g SDBS (Sodium dodecyl benzene sulfonate)/L. The organic solution containing 0.1% (v/v) Tergitol 15-S-3 was gradually added. The resulting CLAs had a creamy appearance. To describe this system, the volume ratio of the dispersed organic phase to the continuous phase was defined as phase volume ratio (PVR).

$$PVR = \frac{\text{Dispersed solvent phase volume}}{\text{Continuous phase volume}} \quad (1)$$

In this study, the value of PVR was maintained at 5. Stable polyaphrons usually show a white creamy appearance and do not cause phase separation for a long time.

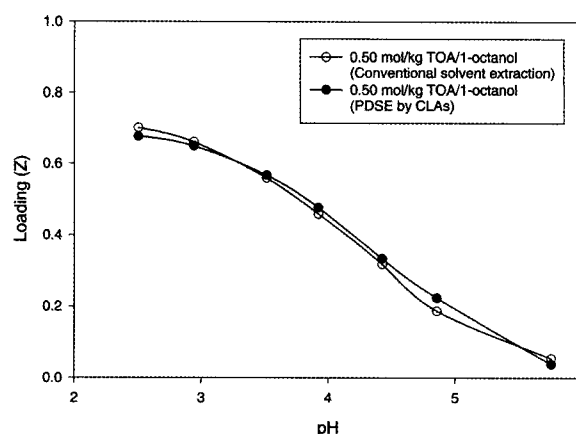


Fig. 2. Effect of pH on the loading values for succinic acid.

### Experimental Procedures in Batch PDSE

Equal volumes (10 mL) of CLAs and an aqueous solution of carboxylic acid were placed in 30-mL vials. The pH value in continuous phase was adjusted with NaOH. To consider the concentration of salts in real fermentation broth, various salts were diluted. Phase mixing was then carried out by hand shaking for 5 sec. For phase separation, mixed-phase samples were centrifuged at 4,000 rpm for 15 min.

Concentrations of succinic 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<sub>2</sub>PO<sub>3</sub> as the mobile phase.

### Stability Measurement of CLAs

CLA stability was measured by their break-up rate [11]. Prepared polyaphrons were transferred into a measuring cylinder. In order to produce CLAs, the continuous phase was gradually added as a destabilizing agent. As usual, the break-up of CLAs in the continuous phase arose from the formation of a film at the amine extractant-continuous phase interface. Amine solvent volume released to surface was recorded against time.

## RESULTS AND DISCUSSION

### Batch PDSE of Succinic Acid

In this study loading is defined as follows:

$$\text{Loading}(Z) = \frac{\overline{C}_B}{C_A^O} \quad (2)$$

where  $\overline{C}_B$  is the concentration of succinic acid extracted into the organic phase and  $C_A^O$  is the initial concentration of TOA.

Fig. 2 shows the effect of pH on the loading values for succinic acid and the comparison of the loading values in PDSE and conventional solvent extraction. For both

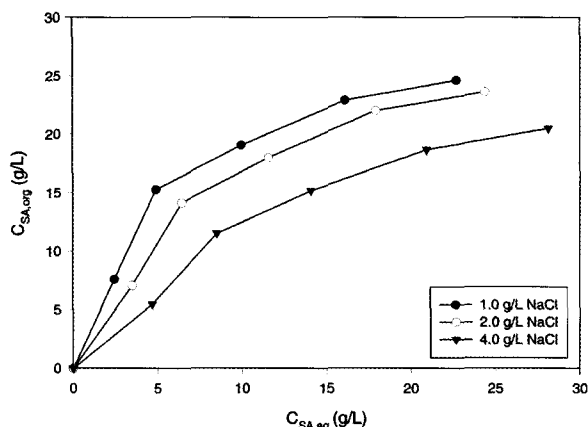


Fig. 3. Effect of concentration of sodium chloride on the extraction equilibrium.

cases, the loading values decreased as pH values increased. A decrease in the value 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 [7]. In particular, there are asymptotic points in each curve near the  $pK_{A1}$  value of succinic acid. We conclude that 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 extractability.

It was also found that the equilibrium data in PDSE was equal to that from conventional solvent extraction in spite of the lack of mechanical mixing in PDSE. This was probably due to the enormous mass transfer area of CLAs.

The effect of salts like sodium chloride and magnesium chloride hexahydrate on extractability was investigated. Fig. 3 represents the effect of sodium chloride concentration on the PDSE for succinic acid using CLAs containing 0.25 mol/kg TOA/1-octanol. Generally, in fermentation process, 1–2 g/L sodium chloride is used as nutrient. Increasing the sodium chloride concentration in aqueous phase caused a decrease in of the extractability of amine for succinic acid. San Martin *et al.* also reported that the presence of sodium chloride decreased the amount of lactic acid extracted by the tertiary amine extractant, Alamine 336 in conventional solvent extraction [15]. This can be explained by assuming that chloride from sodium chloride and  $H^+$  ion from lactic acid yield hydrochloric acid, which is then extracted by the tertiary amine.

The effect of magnesium chloride hexahydrate concentration on the extractability of succinic acid is shown in Fig. 4. The extractability decreases with increasing concentration of magnesium chloride hexahydrate. This result was similar to that observed in the case of sodium chloride. In fermentation broth, 0.2–0.4 g/L magnesium chloride hexahydrate was generally contained. At these concentration ranges, decreases in extractability can be almost negligible due to the low concentration of magnesium chloride hexahydrate.

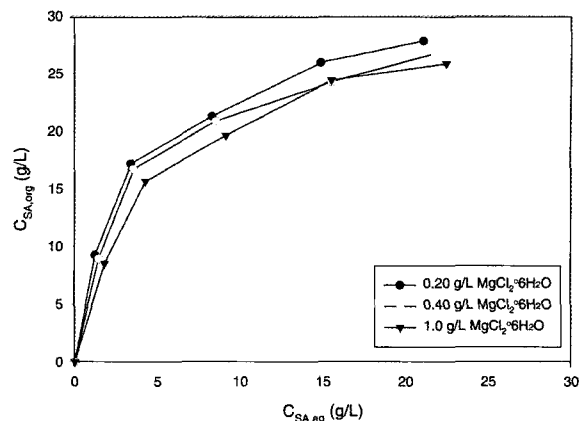


Fig. 4. Effect of concentration of  $MgCl_2 \cdot 6H_2O$  on the extraction equilibrium.

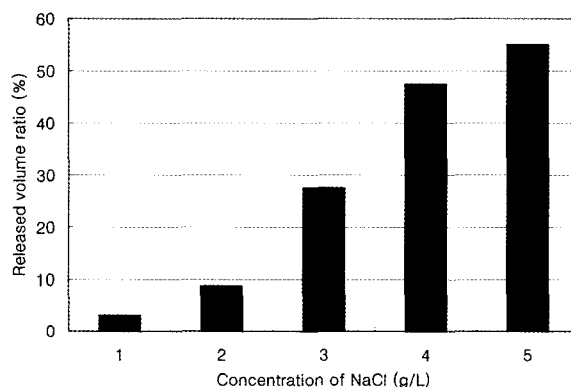


Fig. 5. Effect of NaCl concentration in continuous phase on released solvent volume ratio from CLAs after 3 h.

#### Effect of Salts on the CLA Stability

It was reported that stable CLAs were obtained with CLA formulated with 1-octanol. Even though CLAs could not be formed alone with TOA when SDBS was used as water-soluble surfactant, stable CLAs could be formed with a mixture of TOA/1-octanol [10].

The stability of CLAs can be influenced by various factors: pH, salt species, solvent species, and PVR. Among these factors, salt and pH are important since the CLA stability displays a strong dependence on ionic strength, due to electrostatic interactions associated with the surfactant head-groups. We have already reported that the structure of the CLAs were stable at all pH ranges except under low pH conditions [16].

Fig. 5 shows the effect of sodium chloride concentration in continuous phase on the stability of CLAs made up of 0.25 mol/kg TOA/1-octanol. Released solvent volume from CLAs was measured after 3 h. The stability of CLAs decreased with increasing concentration of sodium chloride, mainly due to electrostatic interaction associated with the surfactant head-groups. Increased salt concentration causes destabilization of CLAs because ionic

**Table 1.** Molecular properties of materials

Material	M.W.	Structure	pK <sub>A1</sub>	pK <sub>A2</sub>	Charge
Succinic acid	118.1	HOOC-CH <sub>2</sub> =CH <sub>2</sub> -COOH	4.21	5.64	-
Trioctylamine	353.66	(CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> ) <sub>3</sub> N	-	-	-
1-octanol	130.23	C <sub>8</sub> H <sub>17</sub> OH	-	-	-
SDBS (Sodium dodecyl benzene sulfonate)	348.5	C <sub>12</sub> H <sub>25</sub> O <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> Na	-	-	Anionic
Tergitol 15-S-3	336	-	-	-	Nonionic

**Table 2.** Half-life of CLAs against various salts contained in continuous phase

	Concentration of TOA dissolved in 1-octanol (mol/kg)		
	0.25	0.50	0.75
0.2 g/L MgSO <sub>4</sub> ·7H <sub>2</sub> O	35.14 hr	36.25 hr	36.25 hr
2 g/L Na <sub>2</sub> SO <sub>4</sub>	63.24 hr	38.80 hr	21.12 hr
0.3 g/L K <sub>2</sub> CO <sub>3</sub>	-	-	261.20 hr
3 g/L (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	≤30 sec	≤30 sec	≤30 sec
0.2 g/L KH <sub>2</sub> PO <sub>4</sub>	≤30 sec	≤30 sec	≤30 sec
0.3 g/L NaH <sub>2</sub> PO <sub>4</sub>	≤30 sec	≤30 sec	≤30 sec

strength depends on the concentration of salt. Considering the normal concentration range of salts in fermentation for succinic acid, the stability of CLAs is sufficient to apply PDSE to real fermentation broth.

Table 2 represents half-life of CLAs in continuous phase containing various salts. Half-life of CLAs was calculated using released solvent volume by pseudo-first order reaction kinetics [17].

$$\ln \frac{V(t)}{V_0} = kt \quad (3)$$

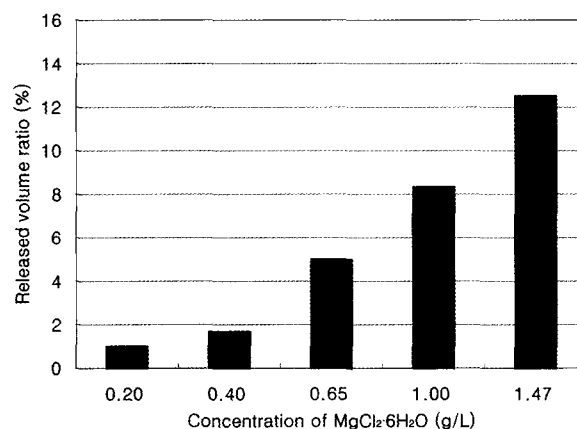
where  $V(t)$  is the remained volume of CLAs,  $k$  is a first order rate constant (time<sup>-1</sup>), and  $t$  is the time elapsed since polyaphron was dispersed. The stability was quantified in terms of a first order half-time ( $t_{1/2}$ ):

$$t_{1/2} = \frac{\ln 2}{k} \quad (4)$$

As seen in Table 2, CLAs were stable in the presence of sodium chloride and magnesium chloride hexahydrate. However, the CLAs were unstable in continuous phase containing other salts.

#### Stripping of Succinic Acid from Organic Phase

Extracted succinic acid should be stripped for the final product form. Generally, the stripping of carboxylic acid in solvent extraction process has been performed by temperature-swing, diluent swing, or pH-swing [18]. The reaction between amine and acid is an exothermic reaction, therefore extraction efficiency decreases with increasing temperature. Diluent swing is based on a shift in

**Fig. 6.** Effect of MgCl<sub>2</sub>·6H<sub>2</sub>O concentration in continuous phase on released solvent volume ratio from CLAs after 3 h.

the equilibrium distribution of the acid from the aqueous phase to the organic phase by changing diluent composition. pH-swing stripping is carried out by using different separation characteristics with pH.

From the results of Fig. 3, it is found that increasing the concentration of sodium chloride decreased extraction efficiency. These results indicate that this method can be used to strip extracted succinic acid from the organic phase as well as for recovering solvent from CLAs as seen in Fig. 5.

#### CONCLUSION

In PDSE process of succinic acid, the equilibrium data

was equal to that in conventional mixer-settler type extraction process in spite of the lack of mechanical mixing in PDSE. In the presence of salts such as sodium chloride and magnesium chloride, the extractability decreases in the function of their concentration but the CLAs were stable. From these results, it is concluded that PDSE process is lesser energy consuming and more rapid process than conventional solvent extraction process and can be successfully applied to real fermentation broth.

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