

# Predispersed Solvent Extraction of Succinic Acid Aqueous Solution by Colloidal Liquid Aphrons in Column

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**Abstract** A study of the PDSE (predispersed solvent extraction) for succinic acid by colloidal liquid aphrons was conducted. The organic phase containing TOA (tri-*n*-octylamine) and 1-octanol permits a selective extraction of succinic acid from its aqueous solution. There was no difference of the extractability of PDSE and that of conventional mixer-settler type extraction. Taking into account the no mechanical mixing in PDSE, it was concluded that the PDSE process is more adaptive than the conventional mixer-settler type extraction process. From mass transfer analysis at the various concentration of TOA in counter-current continuous operation, the concentration of TOA had no influence on the mass transfer coefficient. The loading values in continuous PDSE were almost same as those in batch operation.

**Keywords:** succinic acid, colloidal liquid aphrons, PDSE, mass transfer coefficient

## INTRODUCTION

Succinic acid is an important four carbon dicarboxylic acid, which is used in a wide range of applications such as agriculture, food, medicine, and plastics [1]. Recently, succinic acid has received increasing attention due to its usage as the monomer of polybutylene succinate, a biodegradable polymer.

To date, most of succinic acid is produced petrochemically from *n*-butene through maleic anhydride. However, the biological production of succinic acid by fermentation is in development stage due to the increasing environmental regulation. The succinate fermentation consumes and incorporates carbon dioxide into succinic acid as a carbon dioxide-fixing green technology [2,3].

However, the fermentation broth contains various impurities such as carbon sources, proteins, and other by-products [4]. A downstream process is essential to recover the succinic acid from culture broth. Among several alternatives for the recover of succinic acid, amine-based extraction by reversible reaction has been reported as an efficient recovery process for succinic acid [5-7]. Reactive extraction of succinic acid by amine extractant is based on the acid-base reaction between succinic acid and amine because of its strong basicity. This reaction is ion-pairing reaction in which amine reacts only with undissociated form of succinic acid. The extractability of

amine extractant depends on the degree of dissociation of succinic acid.

Generally, the conventional extraction process includes intensive mixing or considerable contacting time in order to achieve a sufficient mass transfer. The requirements for an extensive time and energy consuming mixer-settler along with a high solvent consumption, are limiting factors for the wide application of conventional solvent extraction. One novel technique that can overcome these drawbacks is the predispersed solvent extraction (PDSE) process [8]. 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 [9]. The structure of CLAs was illustrated in the previous work [10]. Thin soapy films have considerable mechanical strength due to the thermodynamically induced Gibbs elasticity produced by the water-soluble surfactant that is needed for the production of a soapy film. Due to this reason, phases encapsulated by a soapy film are stable [11]. Additionally, CLAs in PDSE can offer higher interfacial area between organic and aqueous phase than conventional dispersion process such as mixer-settler type extractor.

In the present study, the comparison of equilibrium partitioning in PDSE by CLAs and mixer-settler type extractor by straight solvent was performed. Continuous operation of PDSE using column was also carried out. In column operation, the volumetric mass transfer coefficient was calculated and the effect of pH in continuous phase on PDSE was investigated.

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## 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 based on the results of anaerobic fermentation by *Anaerobiospirillum succiniciproducens* [12]. 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).

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

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.

### Experimental Procedure in Batch Extraction by Straight Solvent and PDSE by CLAs

In batch extraction by straight solvent, equal volumes (10 mL) of a straight solvent that contained the tri-*n*-octylamine and diluent and an aqueous solution of succinic 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.

In batch PDSE by CLAs, equal volumes (10 mL) of CLAs and an aqueous solution of succinic acid were placed in 30-mL vials. The pH value in continuous phase was adjusted with NaOH. 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.

### Continuous Operation in PDSE

The schematic diagram of an apparatus is shown in Fig. 1. The internal diameter of the column was 50 mm and its length was 500 mm. Continuous PDSE was carried

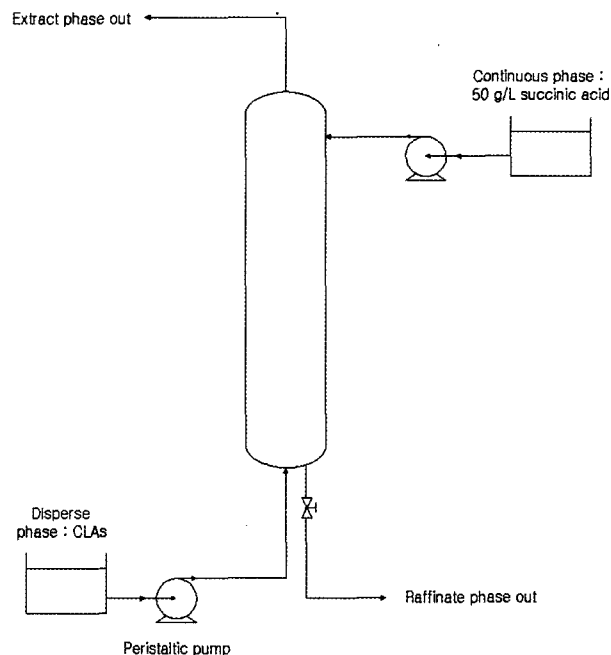


Fig. 1. Schematic diagram of experimental apparatus.

out with succinic acid aqueous solution as continuous phase and CLAs as dispersed phase. The flow rates of both continuous phase and dispersed phase were 0.527 mL/sec. For the first, 900 mL of 50 g/L succinic acid solution was charged into the column. And then, both phases were supplied into the column. Dispersed phase was supplied from the bottom of the column through 10 mm hole and continuous phase was introduced from the top of the column through 10 mm hole. The height of continuous phase was maintained at 460 mm by controlling the flow rate of raffinate phase. For the measurement of succinic acid concentration, raffinate phase was obtained every 10 min or 20 min at the bottom of the column.

## RESULTS AND DISCUSSION

### Batch Extraction of Succinic Acid by CLAs

Fig. 2 illustrates the comparison between the equilibrium curves by CLAs and straight solvent. There was no difference of the extractability of straight solvent and CLAs. The predispersed solvent extraction based on the CLAs is more effective for the separation of succinic acid comparing to the extraction process by straight solvent because of their higher mass transfer rate.

Fig. 3 shows the effect of pH on the distribution coefficient for succinic acid in PDSE by CLAs and mixer-settler type extraction by straight solvent. The distribution coefficient is defined as follows:

$$D_{SA} = \frac{C_{SA}^{org}}{C_{SA}^{raff}} \quad (2)$$

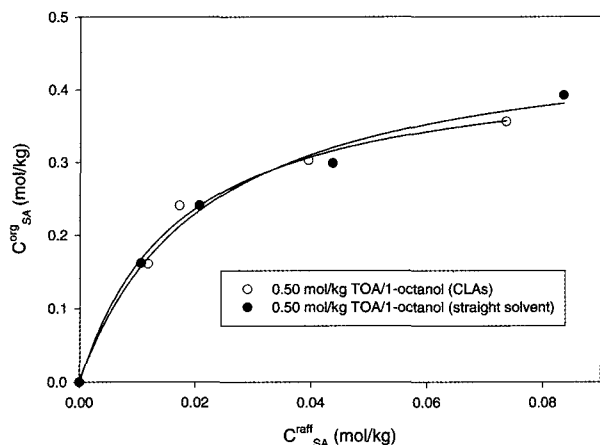


Fig. 2. Comparison of equilibrium curves between PDSE and conventional mixer-settler type extraction.

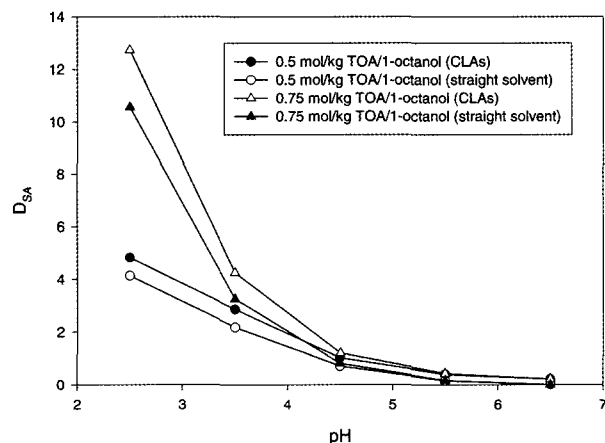


Fig. 3. Effect of pH on the distribution coefficients for succinic acid.

where  $C_{SA}^{raff}$  and  $C_{SA}^{org}$  are the equilibrium concentration of succinic acid in raffinate phase and organic phase, respectively. The concentration of undissociated acid decreases with increasing pH values in aqueous phase. Therefore, this result is consistent with the fact that the undissociated form of the acid is extracted in amine-based extraction process. In this case, there are little difference between PDSE by CLAs and conventional extraction by straight solvent in spite of no mechanical mixing in PDSE by CLAs.

#### Continuous Extraction of Succinic Acid by CLAs in Column

Volumetric mass transfer coefficient was calculated at unsteady-state. Considering the effect of pH on extractability, PDSE in a column was applied to succinic acid solution of various pH. The loading values at steady-state were compared with those at batch operation.

In this study loading is defined as follows:

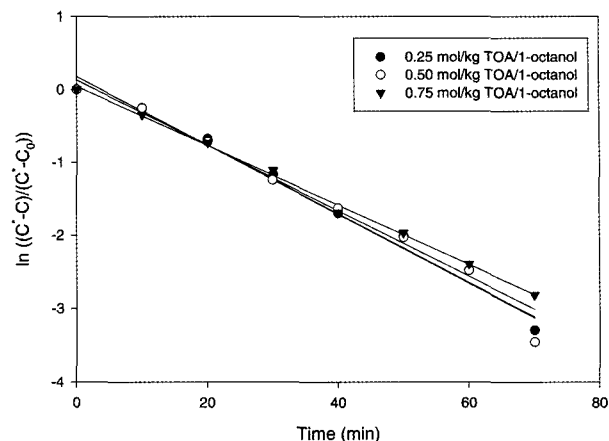


Fig. 4. Unsteady-state data of continuous operation of PDSE using CLAs.

$$\text{Loading}(Z) = \frac{C_{SA}^{org}}{C_{TOA}^0} \quad (3)$$

where  $C_{TOA}^0$  is the initial concentration of TOA.

In continuous phase, mass balance of succinic acid at unsteady-state is given as follows [13]:

$$V_C \frac{dC}{dt} = K_L a V (C^* - C) \quad (4)$$

where  $V_C$  is the volume of continuous phase and  $V$  is the volume of column.

The volume of column  $V$  is represent with the volume of continuous phase  $V_C$  as follows:

$$V = (1 + \phi) V_C \quad (5)$$

where  $\phi$  is the void fraction of the dispersed phase. The void fraction  $\phi$  was 0.0016 in this column. At such a small void fraction, collisions between CLA droplets, and subsequent coalescence, can be ignored during the short duration of the experiment [14]. Hence, the interfacial area was assumed to be constant in this column experiment.

Eq. (4) was integrated from the initial time  $t_0$  and initial concentration of succinic acid  $C_0$  as follows:

$$\ln\left(\frac{C^* - C}{C^* - C_0}\right) = -(K_L a \frac{V}{V_C})(t - t_0) \quad (6)$$

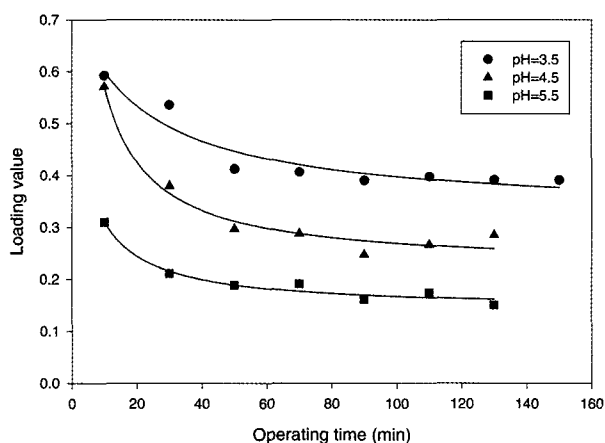
Fig. 4 shows analysis of unsteady-state region of PDSE using Eq. (3). The pH of continuous phase was not adjusted. Volumetric mass transfer coefficient ( $K_L a$ ) values can be calculated from the slope of the plot using following equation:

$$K_L a = \frac{V}{V_C} (\text{slope}) \quad (7)$$

The results are summarized in Table 1. The value of  $K_L a$  is almost same in spite of the variation of TOA con-

**Table 1.** Values of  $K_La$  in column operation of PDSE

	Concentration of TOA dissolved in 1-octanol (mol/kg)		
	0.25	0.50	0.75
$K_La$ ( $\text{min}^{-1}$ )	0.04693	0.04708	0.04065



**Fig. 5.** Loading values of succinic acid in PDSE at various pHs (0.75 mol/kg TOA/1-octanol CLAs).

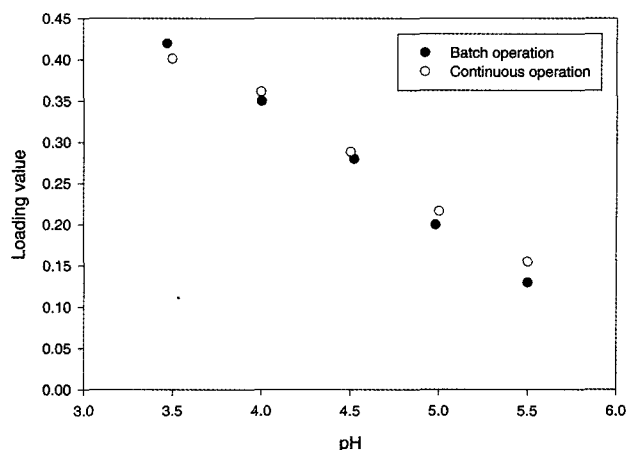
**Table 2.** Values of  $K_La$  in column operation of PDSE at varying of the pH value of continuous phase

pH in continuous phase	$K_La$ ( $\text{min}^{-1}$ )
3.50	0.0820
4.00	0.0728
4.50	0.112
5.00	0.100
5.50	0.0883

centration. The particle size of CLAs can be influenced by the factors such as the stirring rate of CLA preparation, the concentration of water-soluble surfactant, the concentration of oil-soluble surfactant. It was reported that the most important factor was the concentration of water-soluble surfactant, among these factors [13].

The loading values of succinic acid in continuous operation at various pHs were shown in Fig. 5. For all pH values, the loading values reached at steady-state after 50 min of operation. Increasing of pH values causes the loading value to be decreased. A decrease in the values of pH means that the concentration of undissociated acid increased. It was reported that the loading value increases with decreasing values of pH except at extremely high or low pHs, where the loading values do not change significantly [15].

Table 2 shows the variation of volumetric mass transfer coefficient at various pHs in continuous phase. As seen in



**Fig. 6.** Comparison of the loading values in continuous operation at steady state with those in batch operation (0.75 mol/kg TOA/1-octanol CLAs).

Table 2, the volumetric mass transfer coefficient is little affected by pH values.

Fig. 6 shows comparison of the loading value of steady-state at continuous operation with the loading value at batch operation. Through the column experiments, the flow rates of continuous phase and disperse phase were equal. The volume ratio of organic solvent to continuous phase is 0.833. The loading value at continuous phase reached equilibrium value rapidly without any mechanical stirring. From these results, it is concluded that the performance of the continuous operation using PDSE is well over the pH 3 where CLAs are almost stable.

## CONCLUSION

The mass transfer properties of CLA dispersions of TOA/1-octanol in succinic acid aqueous solution have been measured experimentally. The  $K_La$  value was estimated to be about  $4 \times 10^{-2} \text{ min}^{-1}$  and was unaffected by TOA concentration. Continuous PDSE process in column reached at steady-state after 50 min of operation. The loading values in continuous PDSE process were almost same as those in batch process. Therefore, it is concluded that PDSE process is less energy consuming and more rapid process than conventional mixer-settler type extraction process.

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