

Effect of pH on the Extraction Characteristics of Succinic Acid and the Stability of Colloidal Liquid Aphrons

Bong Seock Kim, Yeon Ki Hong and Won Hi Hong^{*}

Department of Chemical & Biomolecular Engineering, Korea Advanced Institute of Science and Technology, 373-1, Guseong-dong, Yuseong-gu, Daejeon 305-701, Republic of Korea

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Abstract—Predispersed solvent extraction (PDSE) by colloidal liquid aphrons (CLAs) was used for the extraction of succinic acid from aqueous solution. The loading values for succinic acid in PDSE by CLAs increased with increasing pH values in aqueous phase. This was due to increasing of the concentration of the undissociated succinic acid. The extractability of PDSE was higher than that of conventional contacting type extraction because of the interaction between factant and acid molecule. The stability of CLAs increased with increasing of the pH values in aqueous phase and decreasing of trioctylamine (TOA) concentration in organic phase. However, the structure of CLAs was stable at all the pH range except very low pH condition.

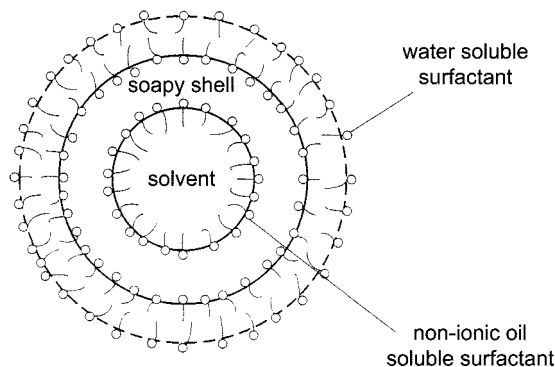
Key words: Amine, CLAs, PDSE, Stability, Succinic Acid

INTRODUCTION

Solvent extractions are used for the purification, enrichment, separation and analysis of various components in mixtures. These are based on the principle that a solute can distribute itself in a certain ratio between two immiscible solvents. Therefore, the selection of both a diluent and extractant determines the equilibrium for a given system, and the efficiency of the extraction process depends on its mass transfer rates. The conventional process includes intensive mixing or considerable contact time in order to achieve a sufficient mass transfer. The requirements for an extensive time, energy consuming mixer/settler, along with a high solvent consumption, are limiting factors for the wide application of conventional solvent extractions. One novel technique that can circumvent these drawbacks is the PDSE (Predispersed solvent extraction) process that employs [Lee et al., 2000].

For the PDSE process, the recent developments in colloidal systems based on phases encapsulated in a thin soap film, and known as aphrons, were achieved. The structures of aphrons are illustrated in Fig. 1. Thin soap 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 soap film. For that reason phases encapsulated in a soap film are surprisingly stable [Sebba, 1989].

Various factors can have an influence on the extractability for succinic acid and the stability of CLAs. Among these factors, the effect of pH was mainly investigated in this study. There is the pH-limitation in reactive extraction by amine extractants. In reactive extraction by amine extractants, reversible complexation between acid and amine is driven by the amount of un-ionized acid in solution and is thereby favored at low pH [Tamada, 1989]. The opti-



Colloidal Liquid Aphron

Fig. 1. Schematic diagram of colloidal liquid aphron.

mal pH for separation by tertiary amine is related to the pK_a of the carboxylic acid. However, in most fermentation processes for producing carboxylic acids except for citric acid, the optimum operating pH is near pH 5-6. Therefore, maintenance of the extractability and the stability of CLAs at this pH range is required for the successful separation process.

Succinic acid is a dicarboxylic acid produced as an intermediate of the tricarboxylic acid cycle (TCA) and also as one of the fermentation products of anaerobic metabolism. Recently, it has received increasing attention due to usage as the monomer of biodegradable polymer such as polysuccinate [Hong et al., 2000, 2002]. Succinic acid is produced from chemical synthesis, the hydration of succinic anhydride, and fermentation [Hong and Hong, 2000]. An efficient and economical downstream purification process is needed for fermentation methods to compete with chemical synthesis because of many impurities such as protein and carbon source from fermentation broth [Zeikus et al., 1999].

In the present work, the effect of pH on the extraction behavior of succinic acid in PDSE by CLAs was investigated and compared with that in conventional mixer-settler type reactive extraction. In

^{*}To whom correspondence should be addressed.

E-mail: whhong@mail.kaist.ac.kr

[†]This paper is dedicated to Professor Wha Young Lee on the occasion of his retirement from Seoul National University.

addition, the stability of CLAs was also measured at various pHs.

EXPERIMENTAL

1. Materials

Succinic acid (99 wt%) was obtained from SIGMA. It was diluted to 50 g/L in aqueous phase, considering the concentration of fermentation broth. It was prepared to various pH values.

TOA, which was purchased from Sigma Co., was used as the extractant without further purification. Diluents were used in reactive extraction of succinic acid because of the high boiling point, the high viscosity, and the corrosive property of TOA. 1-octanol was used as diluent and purchased from Sigma Co.

Water-soluble surfactant for preparing CLAs was sodium dodecylbenzene sulfonate (SDBS). Oil soluble surfactant for preparing CLAs was tergitol 15-S-3. Both of them were purchased from Aldrich Co.

2. Experimental Procedures

CLAs were prepared by the following method. A stable-foam was obtained by mixing of an aqueous phase containing 4 g SDBS/L. To the foaming solution, an organic solution containing 0.01% (v/v) tergitol 15-S-3 was gradually added. 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, PVR was maintained at 5.

After the preparation of CLAs, the PDSE of succinic acid by CLAs was performed. First, the 5 mL solution of succinic acid and CLAs with 5 mL TOA/1-octanol was charged into a 50 mL tube. And then, phase mixing was carried out by hand shaking for 10 sec. For the phase separation, mixed phases were centrifuged at 4,000 rpm for 15 min. The concentration of succinic acid was measured by HPLC with an ion exchange column (Supercogel C-610H, 300 mm×7.8 mm, SUPELCO, USA).

The stability of CLAs on pH was measured as follows.

The 10 mL aqueous solution of various pH values and the CLAs

with 10 mL TOA/1-octanol were mixed by hand shaking 1 time for phase mixing. The released solvent volume from CLAs was used to obtain a measure of stability of CLAs.

RESULTS AND DISCUSSION

1. PDSE of Succinic Acid with CLAs

Fig. 2 shows the effect of pH on the loading value for succinic acid in PDSE by 0.25, 0.50 and 0.75 mol/kg TOA/1-octanol CLAs. The loading value is defined as follows:

$$\text{Loading}(Z) = \frac{C_{SA}^{org}}{C_{amine}^o} \quad (2)$$

where C_{SA}^{org} is concentration of succinic acid in organic phase and C_{amine}^o is initial concentration of amine in organic phase. For all TOA compositions, loading values decrease with increasing pH values. The concentration of undissociated acid increases with pH values. Therefore, this result is consistent with the fact that the undissociated form of the acid is extracted.

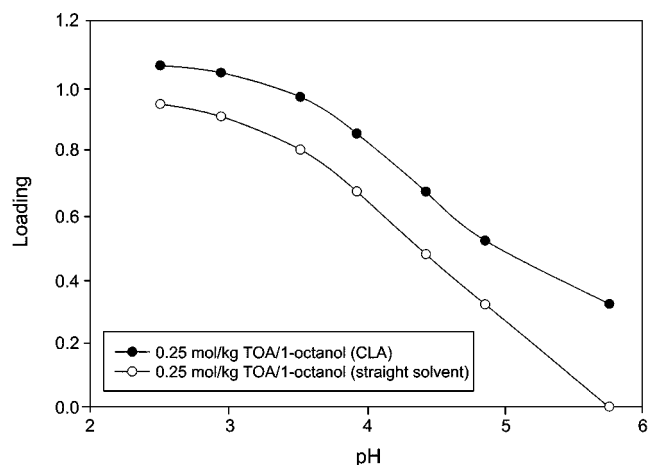


Fig. 3. Comparison of loading value for succinic acid in PDSE and mixer-settler type extraction using 0.25 mol/kg TOA/1-octanol as extractant.

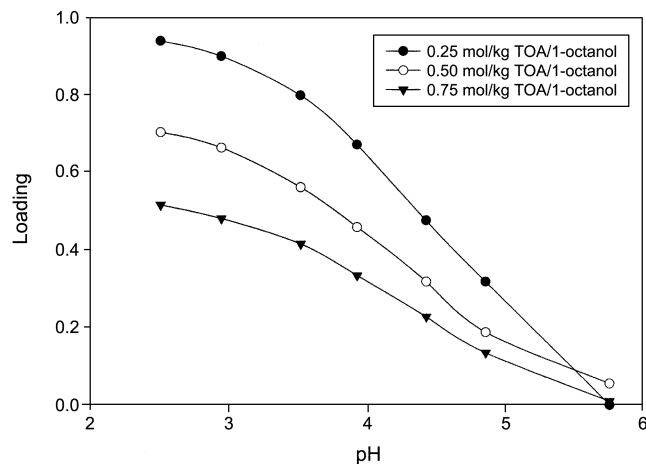


Fig. 2. Effect of the pH in aqueous phase on the loading value for succinic acid.

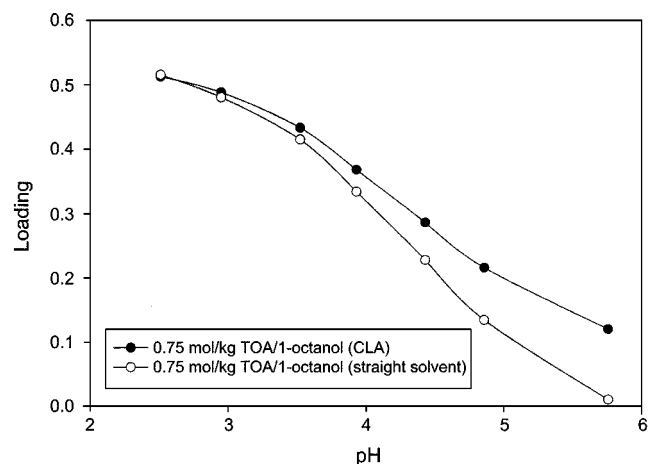


Fig. 4. Comparison of loading value for succinic acid in PDSE and mixer-settler type extraction using 0.75 mol/kg TOA/1-octanol as extractant.

With increasing TOA concentration (decreasing 1-octanol concentration), the loading values decreased. It is concluded that 1-octanol has good solubility for the acid-amine complex due to the hydrogen bonding with the carbonyl oxygen of the complexed acid.

Figs. 3 and 4 show the comparison of the loading values in PDSE and conventional solvent extraction. In Fig. 3, the loading values of PDSE are higher than those of conventional solvent extraction at all tested pH values. In Fig. 4, at the range of low pH, the loading values of PDSE are similar to those of conventional solvent extraction, because almost all the succinic acid was extracted. However, in the range of neutral pH, the loading values in PDSE are higher than those in conventional solvent extraction. One explanation for the higher loading values of PDSE is that there is an interaction between the SDBS and succinic acid molecules. Since the majority of succinic acid molecules will possess a single positive charge, there is the potential for an electrostatic interaction with the negatively charged head-groups of the SDBS molecules. Such an SDBS-succinic acid complex would be preferentially soluble in the organic phase, and consequently enhanced values of loading would be expected [Lye and Stuckey, 2000].

If a cationic surfactant was used in PDSE of succinic acid, no such interaction would be expected. The head-groups of the molecules of cationic surfactants possess a positive charge and would not, therefore, be expected to interact electrostatically with the positively charged succinic acid molecules. In the previous section, the low extractability in PDSE with CLAs by cationic surfactant was observed [Hong et al., 2001].

2. Stability of CLAs with pH

In this section, the effect of pH on the stability of CLAs was mainly investigated. Since the stability of CLAs displays a strong dependence on ionic strength, due to electrostatic interactions associated with the surfactant head-groups, pH should also have an influence on CLA stability [Lye and Stuckey, 1998].

The most stable CLA could be obtained with CLA formulated with 1-octanol. Even though CLAs could 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.

The effect of pH on the stability of CLAs in aqueous phase at 25 °C is shown in Fig. 5. As seen in this figure, the stability of CLAs

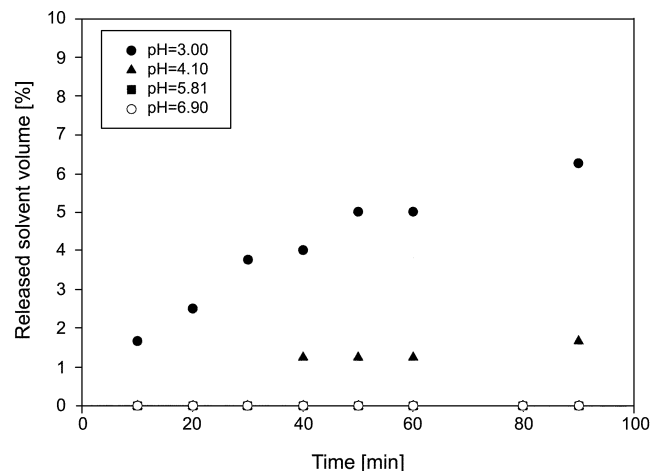


Fig. 5. Effect of the pH in aqueous phase on the stability of CLAs.

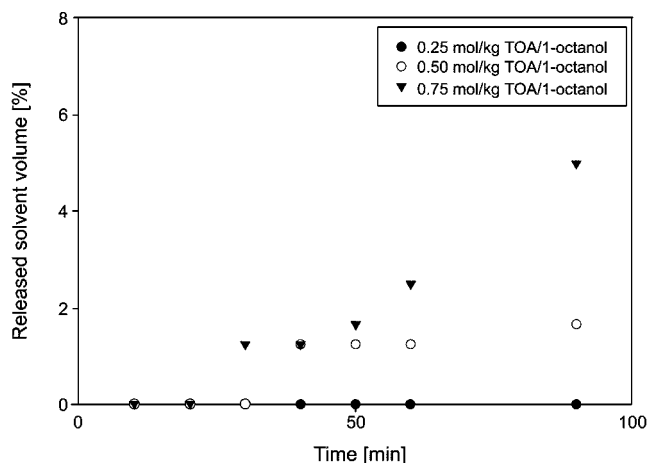


Fig. 6. Effect of the TOA concentration in organic phase on the stability of CLAs (pH 4.10).

increases with increasing pH value. CLAs are stable at near neutral pH for all TOA concentration tested. Even at pH 3, the released solvent volume ratio of CLAs with 0.75 mol/kg TOA/1-octanol is under 10%. At acidic pH, excess hydrogen ions lead to protonation of the head-group of the SDBS located at the outer soapy-shell interface. This would reduce the energy barrier to droplet coalescence and the polarity of the surfactant monomers. At high pH values, CLAs are stabilized by the surface charge repulsion of outer soapy-shell consisted of SDBS.

Fig. 6 shows that the stability of CLA decreases with increasing TOA concentration in the mixture. It is due to the increased basicity of the solvent mixture. Because the organic solvent was surrounded with negative charged surfactant, the CLAs made from the basic solvent were destabilized. Both surfactant and solvent tend to obtain electrons. The stability of CLAs depends both on the PVR and on the composition of solvent of aphrons. Therefore, the stability of CLAs depends not only on the condition of the dispersed phase but also on the composition of organic solvent.

Fig. 7 represents the stability of CLAs at various pHs of aqueous phase and concentrations of TOA after 2 days. It shows that CLAs are stable at near neutral pH and low concentration of TOA. And CLAs with 0.25 mol/kg TOA/1-octanol are almost stable at

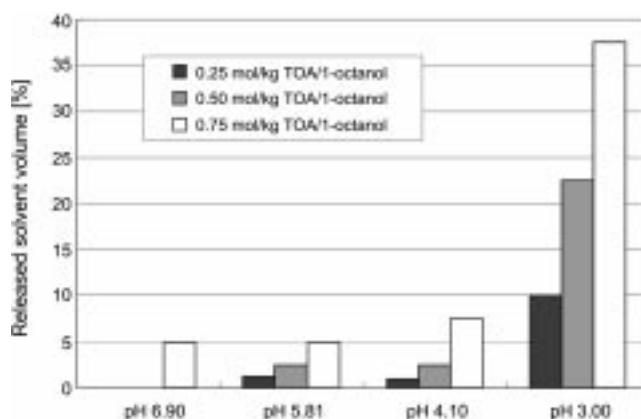


Fig. 7. Stability of CLAs at various pH in aqueous phase and TOA concentration in CLAs after 2 days.

pH 3.00 considering that released solvent volume is 10%.

CONCLUSION

The extractabilities of PDSE of succinic acid by CLAs with TOA/1-octanol decrease with increasing the concentration of amine and the pH value. In the case of pH, the extractabilities decreased dramatically at pH 4.2, the pK_{A1} value of succinic acid. CLAs of 0.50 and 0.75 mol/kg TOA/1-octanol have higher loading values than conventional reactive extraction at near neutral pH. And 0.25 mol/kg TOA/1-octanol CLAs have a higher loading value than conventional reactive extraction at all pH ranges tested. The stability of CLAs decreases with increasing concentration of amine and decreasing pH value. CLAs are stable at near neutral pH range and almost stable over pH 3. It can be proposed that PDSE by CLAs is directly applicable to the extraction of succinic acid from fermentation broth.

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