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Extraction of succinic acid by aqueous two-phase system using alcohols/salts and ionic liquids/salts

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ABSTRACT

Succinic acid is the important feedstock for several industrial products including biodegradable plastics. Production of a fermentation-derived succinic acid (bio-succinic acid) has recently emerged as a potential green technology. For bio-succinic acid production, 50–60% of processing costs are attributed to recovery and purification processes. In this paper, we examine aqueous two phase systems (ATPS) using water-miscible alcohols/salts and ionic liquids/salts to extract succinic acid. From binodal curves, the phase separation abilities of solvents are in the order t-butanol > 1-propanol > HmimBr > 2-propanol $\approx$ OmimBr > BmimBr > ethanol. Extractability of succinic acid was within 0 –72.1% in ATPSs with 1-propanol using salt concentration of 20 g/100 mL-water and depended on the pH of the salt solution. When salts, K_2HPO_4, K_3PO_4, K_2CO_3, KF, $(NH_4)_2SO_4$, $C_6H_5Na_3O_7$, Na_2CO_3, NaCl, $MgSO_4$, and NH_4NO_3, were used, relatively high extractabilities were obtained by using the salt solutions which gave pH smaller than pK_{a1} of succinic acid. In the ATPS with ionic liquids, extractability of succinic acid was within 16–85.5% and were affected by not pH but the salts used. An ATPS with an OmimBr and $(NH_4)_2SO_4$ system gave highest extraction, 85.5%. Extracted succinic acid was quantitatively precipitated by adding sodium hydroxide to the extracted phase and recovered as crystallization of sodium succinate.

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1. Introduction

Succinic acid is the important feedstock for several industrial products including tetrahydrofuran, adipic acid, 1,4-butanediol, aliphatic esters, and biodegradable plastics [1]. Succinic acid for industrial use is mainly produced petrochemically. Nowadays, production of a fermentation-derived succinic acid (bio-succinic acid) has potential as green technology because CO_2 is consumed during the fermentation process [1]. Furthermore, bio-succinic acid has the potential to become a key building block for commodity chemicals [2]. Higher cost in production of fossil fuels results in a high market potential for bio-succinic acid because its production has a net fossil energy consumption of 30–40% less than petroleum-based succinic acid production [3]. A few companies and consortia have begun to develop industrial production of bio-succinic acid [2]. The global bio-based succinic acid market is expected to reach volume of 0.7 million tons by 2020 [4].

In bio-succinic acid production plants reported, membrane and ion exchange as separation processes from the neutralized broth were utilized to obtain the crude succinic acid [5]. In general, for bio-succinic acid production, 50–60% of processing costs are attributed to recovery and purification processes to obtain the final product [3] because succinic acid has relatively low product concentration in the complex medium. Therefore, economical and efficient recovery and purification processes for bio-succinic acid are desired. Several separation methods for succinic acid recovery have been proposed: selective precipitation, adsorption, electrodialysis, extraction with solvents and/or amines, ion exchange, membrane separation and esterification [6,7].

Recently, we proposed liquid membrane systems containing ionic liquid for succinic acid separation [8,9]. Although considerably stable liquid membranes containing ionic liquid were obtained compared with conventional liquid membranes, membrane performance was gradually impaired over the long term. Sun et al. [10] reported an acetone/$(NH_4)_2SO_4$ aqueous two-phase system (ATPS) for recovery of bio-succinic acid.

The ATPS has been well known as one extraction technique for biomolecules [11]. Recent research has focused on ATPSs that were formed by water-miscible organic solvent or ionic liquid with salt [11,12]. Most of the polymers, used in ATPSs so far have high viscosity and tend to form a cloudy solution [13] by the slight external disturbance because of low interfacial tension. Therefore, a polymer/salt ATPS has difficulty isolating the extracted biomolecules from the viscous polymer phase by back-extraction. An ATPS

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composed of hydrophilic organic solvents and salts attracted much attention because of low extraction cost, easy solvent recovery by evaporation and easy scale up [11]. An ATPS composed of hydrophilic ionic liquids and salts was also interesting because of faster phase separation, reduction in viscosity, and tailoring of the polarity of the coexisting phase compared with ATPSs composed of polymers [14].

In this study, we examined water-miscible alcohol/salt and ionic liquid/salt ATPSs for the extraction of succinic acid. As mentioned, water-miscible alcohol is easily recovered by evaporation. 1-Alkyl-3-methylimidazolium bromide was used as ionic liquid. It is known that, because of the different Gibbs energies of hydration of Cl^- (−340 kJ/mol) and Br^- (−315 kJ/mol) [15], the ionic liquids with Cl^- anion hydrate more water molecules than those with Br^-, resulting in difficulty in phase formation as salt was added. Finally we recovered succinic acid from the extracted phase by direct precipitation with alkali hydroxide.

2. Experimental

2.1. Chemicals

1-Butyl-3-methylimidazolium bromide [BmimBr] was purchased from Merck, 1-hexy-3-methylimidazolium bromide [HmimBr] and 1-octyl-3-methylimidazolium bromide [OmimBr] were purchased from Tokyo Chemical Industries, Ltd., and these were used as received. K_2HPO_4, K_3PO_4, K_2CO_3, KF, $(NH_4)_2SO_4$, $C_6H_5Na_3O_7 \cdot 2H_2O$, Na_2CO_3, NaCl, $MgSO_4$, and NH_4NO_3 of G.R. grade were used as salts. 1-Propanol (1-ProOH), 2-propanol (2-ProOH), t-butanol (t-BuOH) and ethanol (EtOH) were used as water-miscible organic solvents.

2.2. Preparation of phase diagram

The binodal curves were determined by turbidimetric titration as described in a previous paper on an ATPS using water-miscible organic solvent and salt [16]. A K_2HPO_4 solution of known concentration was placed in a 100 mL conical flask, and ionic liquids (BmimBr, HmimBr and OmimBr) were added drop-wise to the flask until the clear solution turned turbid or two-phase systems were formed at 25 °C. Then, de-ionized water was added drop-wise to the flask to obtain a clear one-phase system, and more ionic liquids were added again to produce two-phase systems. The composition of this mixture was noted and the experiments were repeated to obtain the binodal curve.

The tie lines were measured by the following procedure. A series of ATPSs with three or four different composition were prepared in graduated glass tubes. These solutions were mixed thoroughly and left standing for more than 1 h in a thermostated bath at 25 °C. To ensure the complete phase separation, these solutions were centrifuged for 10 min at 5000 rpm at 25 °C. After that, visual estimation of volumes of top and bottom phase. The concentrations of organic solvents or ionic liquids were analyzed by HPLC or UV at 211 nm (UV-2500, Shimadzu, Kyoto, Japan), respectively, and the water content in both phases were determined by Karl Fischer's method (AQ-300, Hiranuma, Kyoto, Japan). The salt concentration was calculated by subtracting total weight from weights of water and organic solvent (ionic liquid).

2.3. Extraction of succinic acid using ATPS

Solid inorganic salts and 5 mL of water-miscible organic solvents or ionic liquids were added into the 5 mL solution including succinic acid (20 g/L) to form the ATPS consisting of 25–150 g-salt/100 g-water in a calibrated test tube with a stopper.

The solution was mixed thoroughly and left standing for more than 6 h in a thermostated bath at 25 °C. The volumes of the top and bottom phases were recorded. The concentrations of succinic acid and the water content in both phases were analyzed by HPLC as described in previous papers [8,9] and Karl Fischer's method. The pHs of the aqueous solutions before and after equilibration were determined by a Horiba F-71 pH meter. The extractability (E) and distribution ratio (D) of succinic acid was defined as,

$$E \; [\%] = \frac{C_T V_T}{C_0 V_0} \times 100 \qquad (1)$$

$$D = \frac{C_T}{C_B} \qquad (2)$$

where C and V are the concentration of succinic acid and the solution volume and subscripts T, B and 0 denote the top and bottom phases and initial state.

2.4. Precipitation of succinate from extracted phase

After succinic acid was extracted by ATPS containing ammonium sulfate of 20 g/100 mL, the aliquot of the solvent-rich phase was taken from the test tube for extraction into the flask tube. The precipitants, NaOH, NH_4OH and $Ca(OH)_2$, were added until the precipitate formed. Precipitates were filtered. The amounts of unrecovered succinic acid in the filtrate were measured with HPLC.

3. Results and discussion

3.1. Phase diagram for ATPS consisting of water-miscible organic solvent or ionic liquid, and dipotassium hydrogen phosphate

Fig. 1 shows the effects of water-miscible solvents on the binodal curves of the K_2HPO_4/solvent ATPS at 25 °C plotted as mass fractions. The closer the binodal curves are to the coordinate origin, the less solvent is required for the formation of the ATPS under the same concentration of salt.

From the figure, the phase separation abilities of solvents are in the order t-BuOH > 1-ProOH > HmimBr > 2-ProOH ≈ OmimBr > BmimBr > EtOH. The phase separation abilities of ionic liquids and alcohols with K_2HPO_4 were almost the same as the previous data [15,24]. Pei et al. [15] reported that HmimBr has the best phase-forming ability among the 1-alkyl-3-methylimidazolium
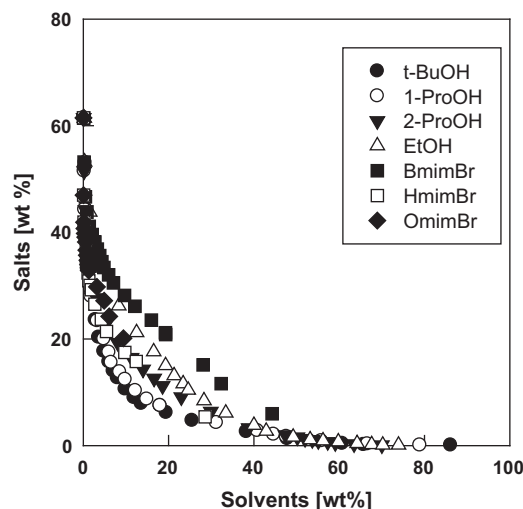

Fig. 1. Binodal curves of solvent (alcohol and ionic liquid) + K_2HPO_4 aqueous two phase system.