Removal of low molecular organic acids from aqueous solutions with reactive extraction

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This paper presents investigation on removal of low molecular organic acids (acetic, lactic, succinic and fumaric) from aqueous solutions with reactive extraction. The results specifically show that the extraction efficiency of acids depends on the type of extractant, diluents of the organic phase and the initial pH of the aqueous phase. It is possible to separate succinic or fumaric from lactic and acetic acids with high selectivity with the use of TOA and Aliquat 336, respectively. Increasing the pH of the aqueous phase results in a reduction of fumaric acid extraction efficiency with solvating extractants. This can be explained by the decreasing share of acidic form, whose extraction is favored by these extractants. Efficient extraction of both fumaric acid and fumarate using Aliquat 336 can be explained by the ionic structure of the quaternary ammonium salt, capable of transporting both forms of the acid.

Keywords: reactive extraction, trioctylamine, tributyl phosphate, Cyanex 923, fumaric, succinic, lactic, acetic acids.

INTRODUCTION

Nowadays organic compounds are obtained more frequently via natural fermentation processes due to the increasing demand for environmentally friendly materials. Biodiesel, produced from vegetable oils and animal fats in transesterification reaction, is the main source of glicerol (a by-product in the process)[1]. Now a bioconversion of glycerol to other required compounds is applied to avoid glycerol purification step and to reduce additional processing costs[2, 3].

As a result of the conversion of glycerol to polyols or dicarboxylic acids (such as succinic or fumaric acid) other low molecular weight organic acids (acetic, lactic, citric acids) are formed in the fermentation broth. They can also be isolated and used in various industries, such as pharmaceutical, chemical and food industry (e.g. as acidity regulators and preservatives). These compounds are particularly attractive due to the possibility of their further conversion to esters, acid chlorides, amines, amides, ketones, aldehydes, etc.[4]. It is necessary to improve manufacturing processes and recovery of these acids, also from waste streams. There are many methods for the separation of acids from fermentation broths, including electrodialysis, nanofiltration, adsorption, ion exchange, or precipitation. Some of these methods generate relatively high costs, moreover, they are not always environmentally friendly because they produce large amounts of solid waste[5].

Reactive extraction is one of the promising methods for the recovery of low molecular weight carboxylic acids. Owing to a suitable extraction system, it is possible to achieve a good selectivity, and high concentration. In addition, extraction does not affect the thermal stability of the reactants, does not require additional energy consumption and retains pollution, and other by-products in the broth[6]. Furthermore, in the case of extraction it is easy to control the pH in the fermentor by continuous removal of the acid, the possibility of recycling the solvent, thus, reducing the amount of waste and reducing the production costs[1]. The previous studies have shown that it is an economical and attractive method for the removal of vast variety of low molecular weight acids i.e. lactic, propionic, succinic, maleic, oxalic, pyridine etc., particularly with the use of organophosphorus extractants, aliphatic amines or quaternary ammonium salts[7–13]. The extraction is a promising method, and its performance is affected by many factors, therefore many efforts are still taken with a view to its intensification.

The studies presented are part of a project aiming at bioconversion of glycerol to other useful products. The fermentation targets on specific production of one particular acid which is accompanied by other species such as carboxylic acids, unreacted glycerol, polyols, e.g. butanodiol, propanodiol. The aim of this study is to present the preliminary results of investigation of the reactive extraction efficiency of selected carboxylic acids from model solutions, and the selection of appropriate process parameters, and also to determine the selectivity of removal of individual acids from the fermentation broths.

EXPERIMENTAL

Reagents

The following extractants (0.1 M solutions) tributyl phosphate (TBP, Fluka), trialkylphosphine oxides (Cyanex 923, Cytec Inc.), trioctylamine (TOA, Fluka), methyltrioctyloammonium chloride (Aliquat 336, Aldrich) were used as received, and were diluted in two different solvents, i.e. octanol (Aldrich) or Exxsol D220/230 (ExxonMobil).

Model aqueous feeds contained from 0.01 to 0.2 M of succinic acid (Suc) and from 0.01 to 0.05 M of fumaric acid (Fum), and 0.05 or 0.1 M of lactic acid (Lact) and acetic acid (Act), respectively. Acid solutions contained 0.1 M NaCl to improve the phase separation. The carboxylic acids were of analytical grade and were purchased from Sigma Aldrich.

Extraction experiments

Extraction studies were carried out from model solutions of individual four carboxylic acids. The extraction was carried out in a typical way in the laboratory

scale at the room temperature, the w/o phase ratio was equal to 1:1, and the samples were shaken from 1 to 60 min. Then the solution was allowed to stand in the glass separatory funnels to achieve complete phase separation. After this time, the aqueous phase was collected and tested depending on the acid examined. The concentration of acids (c_{aq}) was determined using 702 Titrino (Methrom) – NaOH titration (Suc, Act, Lact) or polarograph 797 VA Computrace (Metrohm) (Fum). The pH of the aqueous phase before and after the extraction was measured using Elmetron multifunction meter CX-505 pH electrode. The concentration of acids in the organic phase (c_o) was calculated from mass balance using equation (1), where c_{mod} and c_{aq} are the initial concentration of the acid in model solution before extraction, and the concentration of the acid in the aqueous phase after extraction, respectively.

$$c_o = c_{mod} - c_{aq} \qquad (1)$$

The percentage extraction (%E) and distribution ratio (D) of an acid were calculated according to the following formulas (2) and (3).

$$\%E = \frac{c_o}{c_{mod}} \cdot 100\% \qquad (2)$$

$$D = \frac{c_o}{c_{aq}} \qquad (3)$$

RESULTS AND DISCUSSION

Extraction equilibrium of carboxylic acids

In the first stage of the studies, the time was determined, at which extraction equilibrium of carboxylic acids is established, as shown in Figure 1.
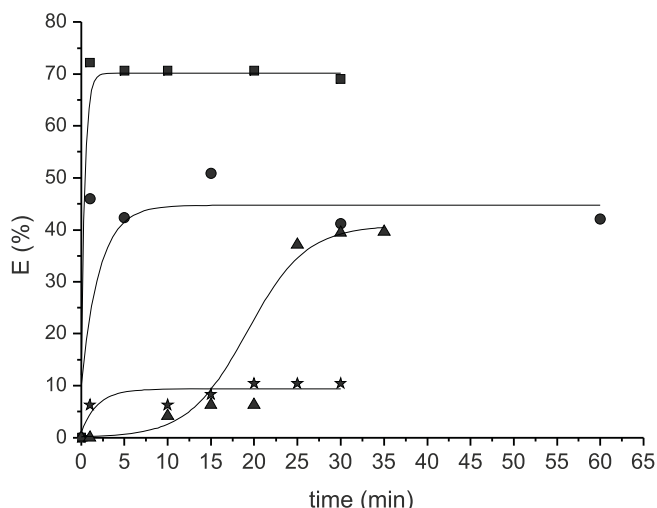

Figure 1. Time of extraction of 0.05 M Fum (■), Suc (●), Act (★) and Lact (▲) with 0.1 M TOA in Exxsol D220/230

When using 0.1 M solution of TOA in Exxsol, the equilibrium of dicarboxylic acids extraction is established fairly quickly. The extraction equilibrium of Lact and Act is established slightly slower (after about 30 minutes), while the efficiency of Lact extraction is higher than Act extraction, and reaches approximately 40%. The order of extraction of the acids studied is in agreement with their acidity and literature data[14], and can be arranged according to the increasing extractability as follows:

Act < Lact < Suc < Fum. The greater the acidity (measured by pK_a, see Table 1) the more effective extraction of the acid by the amine. However, taking into consideration the values of pK_{a1}, lactic acid should be extracted more efficiently than succinic acid. Hence, worse transport of Lact to the organic phase (containing TOA as an extractant) probably results from apparently worse phase separation than in the case of other acids, and in consequence problems with acid determination. Moreover, according to Hano et al.[15] not only does the acidity influence the extraction efficiency but also hydrophobicity of the acids. As Lact is the least hydrophobic (the lowest octanol/water partition coefficient[16]) of the acids studied its association constant with the extractant is smaller than the constant of the other ones. What is more, mono- and dicarboxylic acids differ in their extraction behaviour, e.g. monocarboxylic acids often form complexes in the organic phase with more than one acid per amine, unlike the dicarboxylic ones which react rather with one molecule of amine[14, 17, 18].

Diluents for the organic phase

The nature of the diluent of the organic phase is an important factor influencing the formation of acid-amine species in the organic phase, and consequently the efficiency of acid extraction[8, 14, 18]. Thus, the selection of a suitable diluent for the organic phase enhances extractant effectiveness. On this basis, the studies have been carried out using octanol (an active diluent) and Exxsol D220/230 (mixture of aliphatic hydrocarbons; a passive diluent). Figures 2 and 3 show the isotherms of Lact and Act and Figures 4 and 5 present the isotherms
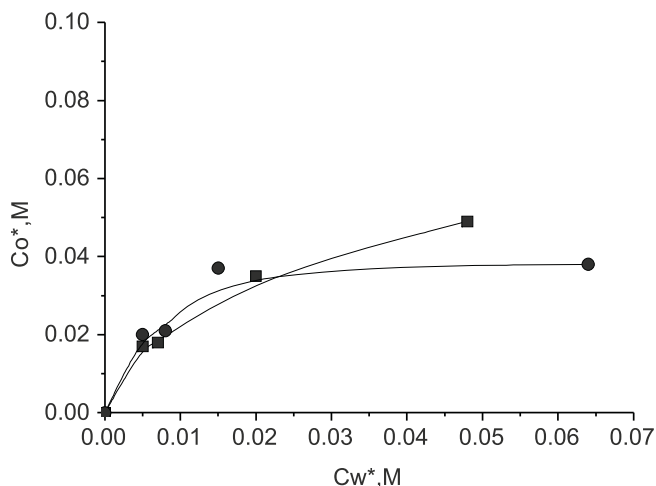

Figure 2. Extraction isotherms of Act for various diluents, aqueous phase: 0.1 M acid, 0.1 M NaCl, pH_i 2; organic phase: 0.1 M extractant TBP in Exxsol (■) or in octanol (●)

of Suc and Fum acids, depending on the type of the diluent used.

Octanol has been selected for further studies, as an active diluent which supports activity of extractants by enhancing solvation of acid-amine ion pairs[15, 17], and extraction with organic phases containing this diluent is more effective than with Exxsol D 220/230.
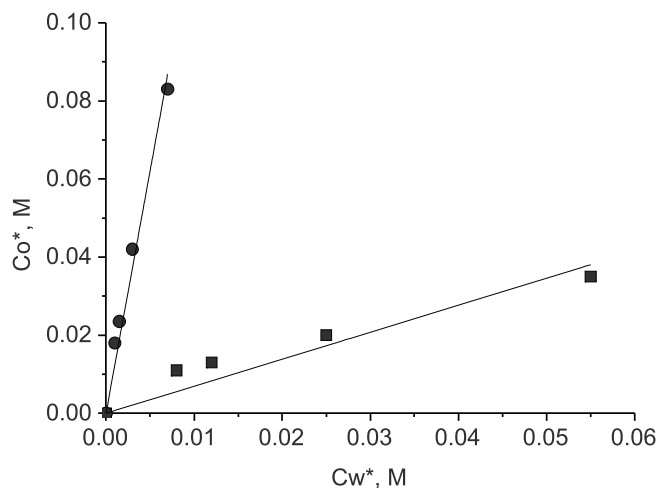
Figure 3. Extraction isotherms of Lact for various diluents, aqueous phase: 0.1 M acid, 0.1 M NaCl, pH_i 2; organic phase: 0.1 M extractant TBP in Exxsol (■) or in octanol (●)
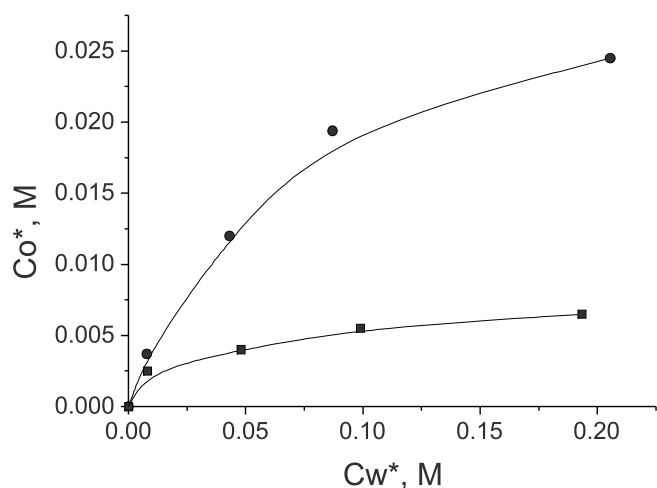

Figure 5. Extraction isotherms of Fum for various diluents, aqueous phase: 0.1 M acid, 0.1 M NaCl, pH_i 2; organic phase: 0.1 M extractant TBP in Exxsol (■) or in octanol (●)

Figure 4. Extraction isotherms of Suc for various diluents, aqueous phase: 0.1 M acid, 0.1 M NaCl, pH_i 2; organic phase: 0.1 M extractant TBP in Exxsol (■) or in octanol (●)

Figure 6. Isotherms of Suc extraction with Cyanex 923 in octanol, pH 2.5 (■); pH 6 (●); pH 9 (▲)

The pH effect

The effect of pH in the range from 2.5 to 9 on the extraction efficiency of Suc and Fum with various extractants has been examined. The crucial issue to consider pH influence on possibility of acids' extraction is their dissociation. Dissociation constants for the acids studied are given in Table 1.

Figures 6 and 7 show the exemplary extraction isotherms of Suc and Fum with solvating extractant Cyanex 923 diluted in octanol.

The isotherms of Suc extraction, independently of pH value, have curved course, and Fum experimental points form a straight line. The extraction isotherms of
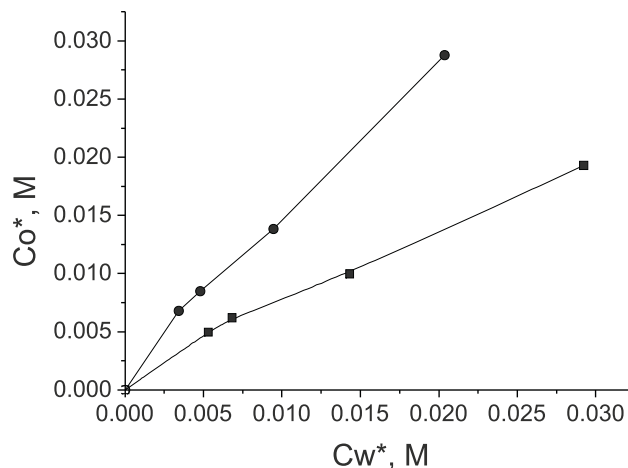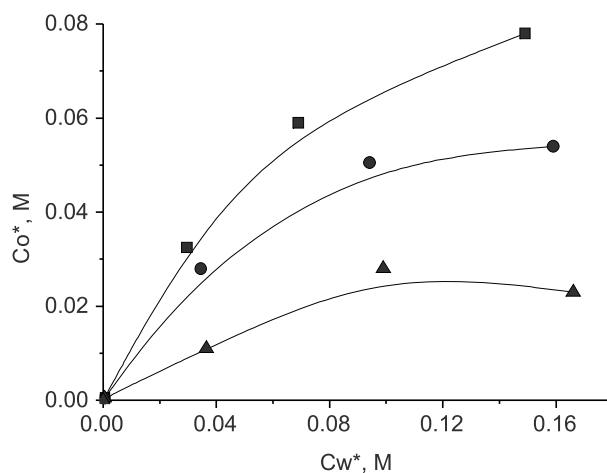
Fum do not achieve plateau, which indicates that Cyanex 923 could extract much more Fum. However, extraction of this acid is limited by its solubility in water (4.9 g/dm³)[19].

Noticeable is the significant effect of the pH value on the extraction efficiency, which is associated with the transition of the acid to the basic form with the increase in pH. The highest extraction efficiency of Suc amounts to about 50% at initial pH of the aqueous solution equal 2.5. The value of percentage extraction means that the extracted acid-Cyanex 923 species form 1:2 ion pairs in the organic phase. In the conditions analysed, an increase in pH from 2.5 to 9 causes a decrease in the extraction efficiency of about 50% due to the fact that solvating extractants transport acid according to the reaction of solvation of dicarboxylic acid molecule:

Table 1. Dissociation constants for the mono- and dicarboxylic acids studied[11]

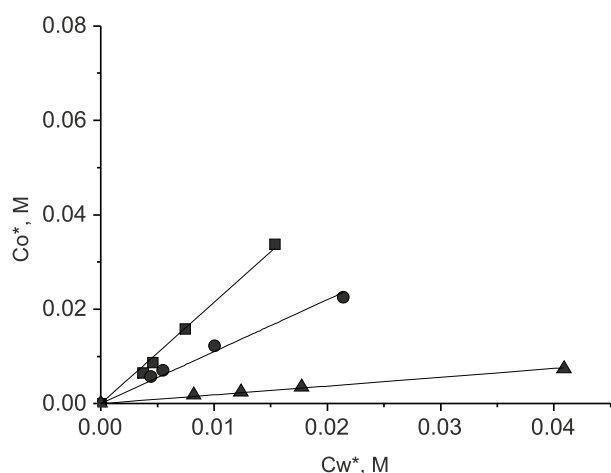| Lactic	Acetic	Fumaric	Succinic
$pK_a = 3.85$	$pK_a = 4.76$	$pK_{a1} = 3.02$ $pK_{a2} = 4.38$	$pK_{a1} = 4.21$ $pK_{a2} = 5.64$

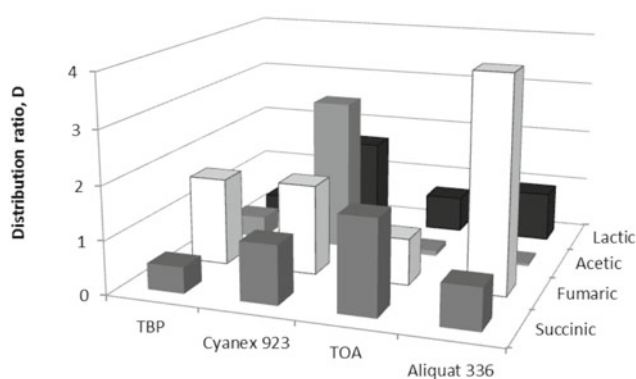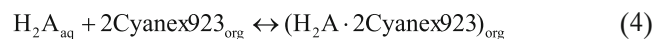**Figure 7.** Isotherms of Fum extraction with Cyanex 923 in octanol, pH 2.5 (■); pH 6 (●); pH 9 (▲)

Figure 8. Distribution ratio of the acids studied between the organic phase with various extractants and the aqueous phase of the initial pH 2

$$H_2A_{aq} + 2Cyanex923_{org} \leftrightarrow (H_2A \cdot 2Cyanex923)_{org} \qquad (4)$$

Thus, with increasing pH (decreasing contribution of the acidic form) the extraction of Suc and Fum decreases.

The summary of the studies is presented in Figure 8. The distribution ratio of the various acids between the organic and aqueous phase varies depending on the extractant type (octanol as a diluent). Very good extraction efficiency is achieved for monocarboxylic acids (Act, Lact) with Cyanex 923, while for the dicarboxylic acids Fum and Suc the best are basic extractants Aliquat 336 and TOA, respectively. The differences in extraction efficiency are due to the nature of extractants applied and formation of various complexes extractant-mono- or dicarboxylic acid.

Usually fermentation broth from glycerol bioconversion contains, besides polyols, succinic or fumaric acid accompanied by lactic and acetic acids[20]. It would be recommended to separate dicarboxylic acids from monocarboxylic ones and the rest of compounds. Our results for individual acids indicate that basic extractants allow for almost complete rejection of acetic acid. Thus, TOA quite selectively extracts Suc, while Aliquat 336 – Fum. Differentiation of the extraction efficiency in relation to the various acids allows to design a method for the separation of various acids with a multi-stage reactive extraction.

CONCLUSIONS

Reactive extraction allows effective removal of the selected carboxylic acids from the aqueous phase. The effectiveness of this technique depends on:
– the type of extractant – the most effective extractants proved to be the basicones (TOA and Aliquat 336) for dicarboxylic acids, and a solvating one (Cyanex 923 for monocarboxylic acids;
– type of a diluent used – octanol, as an active diluent, increases the effectiveness of the extractants studied;
– pH value of solutions, dissociation of an acid in the aqueous phase.

The studies carried out with model solutions of individual acids will serve further experiments associated with selective separation of various acids from fermentation broths.

ACKNOWLEDGMENT

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