

SELECTIVE SEPARATION OF DICARBOXYLIC ACIDS BY REACTIVE EXTRACTION

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ABSTRACT. In this paper the studies on separation of some dicarboxylic acids (oxalic acid, malonic acid, succinic acid and adipic acid) by reactive extraction with Amberlite LA-2 in butyl acetate were continued. Thus, the conditions for a selective extraction were settled. The individual selective extraction is not possible because of the comparable values of acidic constants for oxalic and malonic acids, on the one hand, and for succinic and adipic acids, on the other hand. In this case, only selective extraction of oxalic and malonic acids can be achieved.

For a high selectivity, both a molar ratio of 0.9 - 1 between the strong dicarboxylic acids (oxalic and malonic acids) and the extractant and a concentration of Amberlite LA - 1 lower than the stoichiometric value for all acids extraction are required.

INTRODUCTION

Since 1970 the advantages offered by the reactive extraction determined the extension of the applications area towards the separation of organic compounds. In present, the conditions for reactive extraction of some derivatives, namely : carboxylic acids, amino acids, phenolic derivatives, alcohols, antibiotics, are intensively studied with the purpose of industrial scale application [1].

In the previous works the mechanism, the limiting steps and the kinetic of the reactive extraction of some dicarboxylic acids (oxalic, malonic, succinic and adipic acids) by Amberlite LA-2 in butyl acetate have been settled [2]. The aim of this paper is to study the possibility of selective separation of these acids by extraction. The technique which was used is dissociative extraction, based on the difference between their acidity. This technique has been used on selective separation of some isomer organic bases having different basic capacities by reactive extraction with a strong mineral acid [3, 4].

EXPERIMENTAL PART

The experimental studies have been carried out in two separate stages. The first one consists of the preliminary study on selective extraction of oxalic, malonic, succinic and adipic acids. The laboratory equipment used includes a modified extraction cell of the Lewis type described in the pervious papers [2]. The studies were carried out in a continuous system, the aqueous phase and the organic phase being separately fed and mixed by means of two perforated blade stirrers with variable rotation speed (0 - 1000 rpm). The two phases throughputs were: 1.6 l/h for aqueous phase and 2.15 l/h for solvent phase. The initial concentrations of dicarboxylic acids in aqueous solution were : oxalic acid 1.53 and 4.83 g/l, malonic acid 1.50 and 4.77 g/l, succinic acid 1.57 and 5.07 g/l, adipic acid 1.53 and 4.73 g/l.

Stamps prelevation has been carried out from the aqueous phase evacuation tract.

The second stage represents the study on these organic acids extraction in a glass column provided with a vibratory mixer [5, 6]. In this case, a very high interfacial area and a high mass transfer rate have been obtained. The volume ratio between the aqueous phase and solvent phase was 1, each phase volume being of 50 cm³. The acids initial concentrations in aqueous solution were : oxalic acid 0.92 - 4.60 g/l, malonic acid 1.06 - 5.30 g/l, succinic acid 1.10 - 5.51 g/l, adipic acid 1.00 - 5.02 g/l.

After the mixing of the two phases for 1 minute, the resulting emulsion was separated in a centrifugal separator at 5000 rpm.

In both experiments the organic phase was butyl acetate with a content of 20 g/l Amberlite LA-2 .

The extraction process development has been followed by pH - metric titration of initial aqueous solution and raffinate with a sodium hydroxide solution of 1.74.10⁻² N and 3.10⁻² N respectively, and by analyzing the obtained curves.

RESULTS AND DISCUSSIONS

As a function of their acidity the dicarboxylic acids studied can be grouped in two categories: oxalic and malonic acids, on the one hand, and succinic and adipic acids, on the other hand, as can it be observed from the Table 1 [7]. The possibility of the individual selective extraction is repressed by the presence of this difference between the two groups and by the comparable acidity values for the organic acids existed in the same group, determining the selective extraction of oxalic and malonic acids. Although this phenomena represents the main characteristic of this extraction system, the separation selectivity has been strongly depended by the acids overall concentration in the initial aqueous solution, or by dicarboxylic acids and Amberlite LA-2 molar ratio, respectively.

The variation of the specific mass flow for oxalic and malonic acids and for succinic and adipic acids, as well as the variation of the selectivity factor, calculated as the ratio of these two specific mass flows, with the rotation speed have been followed in the preliminary studies.

Table 1.

Values of the acidic constants for the extracted dicarboxylic acids.

Dicarboxylic acid	k_1	k_2
Oxalic acid	$6.5 \cdot 10^{-2}$	$6.1 \cdot 10^{-5}$
Malonic acid	$1.4 \cdot 10^{-2}$	$8.7 \cdot 10^{-7}$
Succinic acid	$6.9 \cdot 10^{-5}$	$2.8 \cdot 10^{-6}$
Adipic acid	$3.7 \cdot 10^{-5}$	$3.9 \cdot 10^{-6}$

For low initial concentrations of dicarboxylic acids in aqueous solution an increase of the specific mass flows can be observed, the increase being significantly for the strong acids, especially (Figure 1).

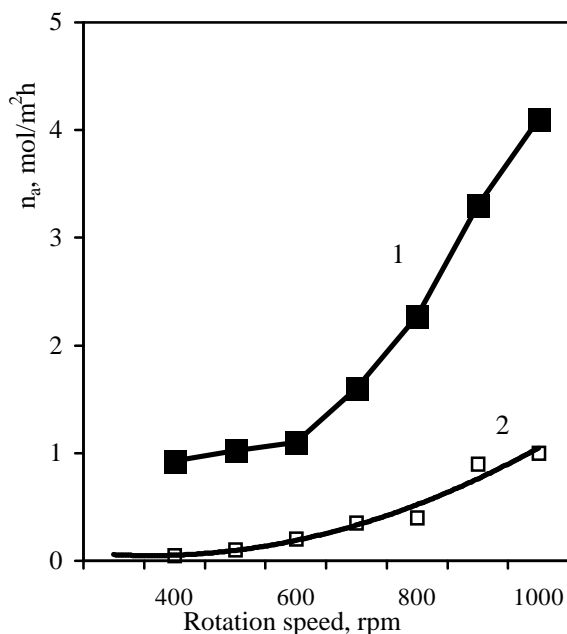


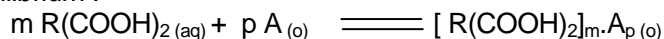
Figure 1. Specific mass flow, n_a , versus rotation speed (1 - oxalic and malonic acids, 2 - succinic and adipic acids; initial concentrations: 1.53 g/l oxalic acid, 1.50 g/l malonic acid; 1.57 g/l succinic acid, 1.53 g/l adipic acid).

The weak acids, succinic acid and adipic acid, cannot be extracted for rotation speeds below 400 rpm. In this case, the selectivity factor has an infinite value and then decreases to a value of 3.14 corresponding to a rotation speed of 1000 rpm (Figure 2, curve 1).

Increasing the initial acids concentration a change in extraction process evolution has been observed, namely the increase in the specific mass flow for oxalic and malonic acids. In the same time, it was observed that a constant value of the specific mass flow for succinic and adipic acids was obtained, disregarding the increase of rotation speed (Figure 3).

The difference in extraction system behaviour is the result of the change in reactive extraction mechanism by changing the acids initial concentration combined with the influence of the diffusion towards the contacting interface.

The reactive extraction mechanism can be expressed by following interface equilibrium :



where $R(\text{COOH})_2$ is the dicarboxylic acid and A is the extractant of Amberlite LA-2 type.

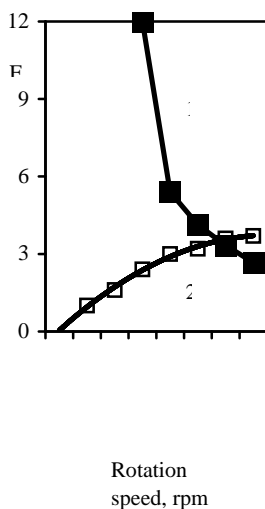


Figure 2. Variation of selectivity factor, F , with rotation speed.

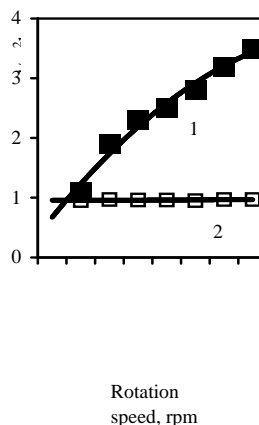


Figure 3. Specific mass flow, n_a , versus rotation speed (1 - oxalic and malonic acids, 2 - succinic and adipic acids; initial concentrations: 4.83 g/l oxalic acid, 4.77 g/l malonic acid, 5.07 g/l succinic acid, 4.73 g/l adipic acid).

For a constant value of the extractant concentration, the structure of the formed complex is determined by the level of the organic acid concentration, as follows :

- a. for a molar ratio between
- b. for a molar ratio nearly 1, the extraction system components react in a equimolecular proportion forming : $R(\text{COOH})_2.A$;
- c. at high initial concentration of the organic acids, a third phase of high complex concentration can appeared in non - polar diluents (butyl acetate, for example). In this case, the structure of the complex is $[R(\text{COOH})_2]_m.A_p$ [8]. For a molar ratio greater than 1 this complex can be formed, too.

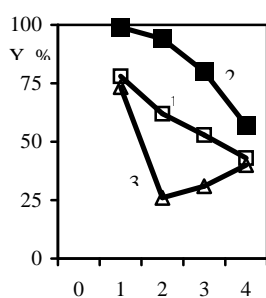
In the first series of experimental studies the extraction mechanism was **a.**, owing to the molar ratio between dicarboxylic acids and extractant of 0.8. For a diffusional regime, at low rotation speed, the interfacial concentration of the extractant is low, below the stoichiometric necessity, thus reacting with the strong acids especially. By increasing the rotation speed the extractant concentration at the interface is increased, becoming greater than the requirement for oxalic and malonic extraction only. The results consists in the increase in mass flow of weak acids, succinic acid and adipic acid.

At the initial concentration of the acids greater than former, for a molar ratio between dicarboxylic acids and Amberlite LA-2 of 3.3, the formation of complexes of **c.** type is possible, even at very low rotation speed level. The rotation

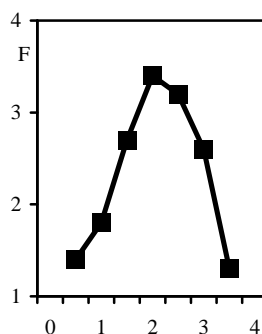
speed increase, respectively the diffusion rate increase, determines the increase in interfacial concentration of the extraction system components. According as the strong acids reach the interface the extractant will preferential react with them.

From these data the following conclusion can be drawn : the extractant concentration in organic phase must be lower than the stoichiometric necessity for all dicarboxylic acids extraction and the value of the molar ratio between strong acids (oxalic and malonic acids) and Amberlite LA-2 must be nearly 1 for a high selectivity of reactive extraction process.

The results obtained in extraction column with vibratory mixer have been confirmed the earlier conclusions. By increasing the overall acids concentration in aqueous solution, respectively by increasing the molar ratio value between the acids and the extractant from 0.68 to 3.43, the decrease of the reactive extraction yield for oxalic and malonic acids from 100 % to 53.05 % has been observed. The reactive extraction yield for succinic and adipic acids decreases to a minimum value of 26.77 %, then increasing to 35.33 %. The overall extraction yield has been linearly reduced by increasing the acids concentration (Figure 4).



M



M

Figure 4. Influence of molar ratio M between dicarboxylic acids and extractant on reactive extraction yield, Y (1 - overall extraction yield, 2 - oxalic and malonic acids extraction yield, 3 - succinic and adipic acids extraction yield).

Figure 5. Variation of selectivity factor, F, with molar ratio, M.

The selectivity factor, calculated as ratio of the extraction degrees of the two acid groups, had a particularly evolution, reaching a maximum of 3.45 for a value of ratio between the total acids moles and extractant moles of 1.71, and for a molar ratio between strong acids and extractant of 0.95, as can be seen from Figure 5.

The selectivity factor maximum value corresponds to the extraction degree minimum value for the weak acids.

CONCLUSIONS

The obtained data indicate the possibility of the oxalic and malonic acids selective separation by dissociative extraction with Amberlite LA-2 in butyl acetate by means of the difference on acidic constants. However, the individual selective extraction cannot be achieved because of the small differences between the acidity of each acid group components.

Using a molar ratio between the strong acids and Amberlite LA-2 of 0.9 - 1, concomitant with an extractant concentration less than the requirement for total acids extraction, a high selectivity value can be reached.

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