SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY
SOUTH. BRAZ. J. CHEM., Vol. 5, N° 5, 1997

REACTIVE EXTRACTION OF DICARBOXYLIC ACIDS
I. MECHANISM, LIMITING STEPS AND KINETICS

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ABSTRACT. In this paper the reactive extraction of some dicarboxylic acids (oxalic acid, malonic acid, succinic acid, glutaric acid and adipic acid) have been studied. These acids have been extracted by Amberlite LA-2 in butyl acetate using a modified extraction cell of the Lewis type. Mechanism, limiting steps and kinetic of the mass transfer process have been settled.

RESUMO Foi estudada a extração reativa de alguns ácidos dicarboxílicos (oxálico, malônico, succínico, glutárico e adípico). Estes ácidos foram extraídos com Amberlite LA-2 com acetato butílico e usando uma célula de extração modificada do tipo Lewis. Foram determinadas as etapas determinantes, o mecanismo e a cinética do processo de transferência.

KEYWORDS : dicarboxylic acids, oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, reactive extraction, Amberlite LA-2.

DOI: 10.48141/SBJCHEM.v5.n5.1997.95_1997.pdf

INTRODUCTION

Since 1970 the advantages offered by the reactive extraction have been determined the extent of applications area on organic compounds separation. In present, the conditions for reactive extraction of some derivatives, namely : carboxylic acids, amino acids, phenolic derivatives, alcohols, antibiotics, are intense studied with a view to industrial scale applying [1].

For the carboxylic acids separation by reactive extraction different extracting agents have been used :

- organophosphoric agents (tri-n-octyl phosphine oxid, tri-n-butyl phosphate) [2-5] ;
- high molecular weight aliphatic amines or amines salts, especially secondary and tertiary amines (lauryl-trialkylmethylamine, named Amberlite LA-2, ditridecylamine, named Adogen 283, tri-n-octylamine, tri-iso-octylamine, named Adogen 381, tri-n-(octyl - decyl)-amine, named Alamine 336, tri-n-octyl-methyl ammonium chloride, named Adogen 464) [2,5-15].

The carboxylic acids extraction mechanisms are influenced by extraction system nature, being based on a chemical reaction of solvation or ionic exchange type or on a formation of high molecular weight ion - pair compounds.

In this paper the reactive extraction of the series of dicarboxylic acids : oxalic, malonic, succinic, glutaric and adipic acids, by Amberlite LA-2 in butyl acetate medium is studied, with a view to establishing the mechanism, the limiting steps and the kinetic of mass transfer process.

EXPERIMENTAL

The experimental studies have been made in two separate stages. The first one consists on the study on the reactive extraction mechanism by means of equilibrium data. The extraction was carried out in batch system in a cylindrical glass vessel, provided with a jacket which the thermosetting agent passes, namely ethylene glycol maintained at 24°C.

The initial concentration of dicarboxylic acids in aqueous phase has been varied as follows :

- oxalic acid : 1.80 - 71.66 g L^{-1};
- malonic acid : 3.43 - 65.33 g L^{-1};
- succinic acid : 4.55 - 54.10 g L^{-1};
- glutaric acid : 5.49 - 81.99 g L^{-1};
- adipic acid : 3.11 - 11.18 g L^{-1}.

The organic phase was butyl acetate with a content of 42 g L^{-1} Amberlite LA-2. The volume ratio between the aqueous solution and the solvent phase was 1, each phase volume being 25 mL.

The second stage consists in the establishment of the nature of the resistances which can appear in the organic acid overall mass transfer process and the study on reactive extraction kinetic. The laboratory equipment used includes a modified extraction cell of the Lewis type (Figure 1). The extraction cell was made up of two compartment of glass pipe having 750 mL each. The phases have been mixed by two perforated blade stirrers with variable rotation speed (0 - 1000 rpm). The contacting area of the central circular interface was 28.27 cm^2.

The studies on the limiting steps were carried out in a continuous system, the aqueous phase and the organic phase were separately feed, and the two phases throughputs were :

- aqueous phase : 1.25 - 2.73 L h^{-1};
- organic phase : 1.23 - 2.40 L h^{-1}.

Stamps prelevation was carried out from the aqueous phase evacuation tract.

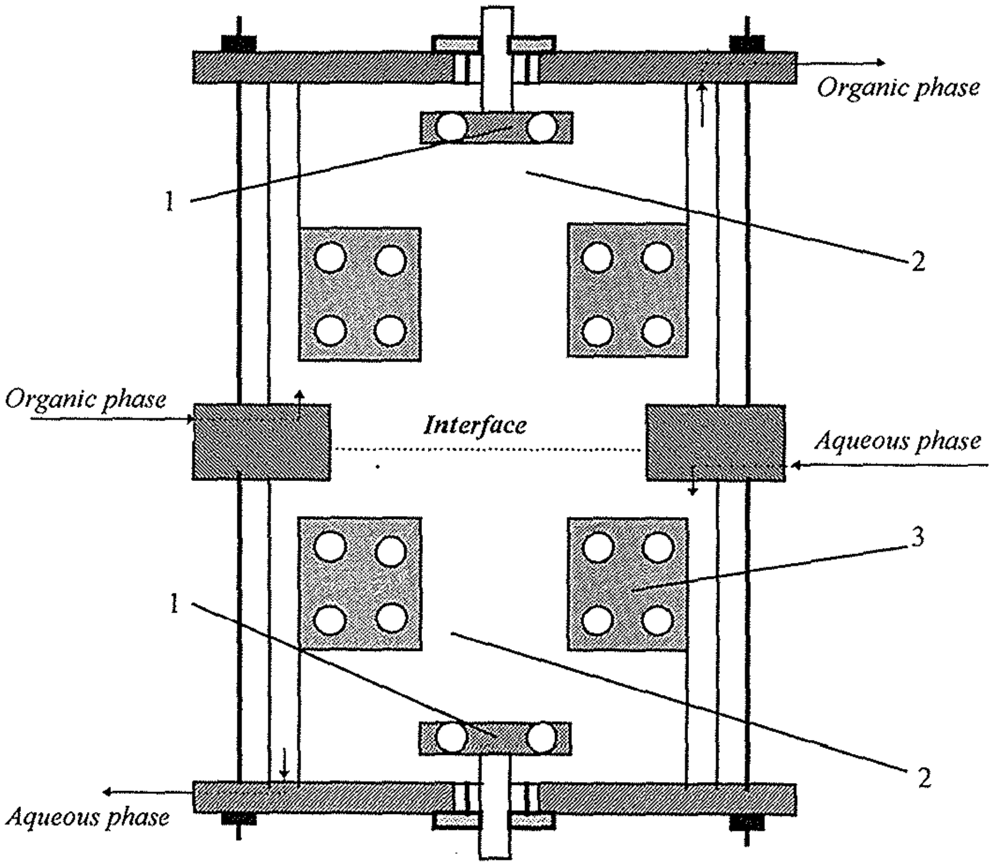

Figure 1. Extraction cell (1 - cylindrical compartment, 2 - perforated blade stirrer, 3 - baffle).

The reactive extraction kinetic was established in a batch system, at 24°C, for kinetic regime (rotation speed value greater than 1200 rpm, level determined by means of preliminary studies). Thus, the rotation speed values were between 1.600 and 1.800 rpm for each phase.

The extracting agent concentration in butyl acetate was 80 g L^{-1} for the study on limiting steps and 42 g L^{-1} for the kinetic study. In both experiments the initial concentration of dicarboxylic acids was 4.50 - 6.78×10^{-2} M.

The extraction process development has been followed by titration of initial aqueous solution and raffinate with a sodium hydroxide solution of 3×10^{-2} M.

RESULTS AND DISCUSSION

a. *Reactive Extraction Mechanism*

The reactive extraction of dicarboxylic acids by Amberlite LA-2 can be described by following interface equilibrium :

$$m\,R(COOH)_{2\,(aq)} + \;p\,A_{(o)} \rightleftharpoons [\,R(COOH)_2]_m.A_{p\,(o)}$$

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

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 dicarboxylic acid and Amberlite LA-2 below 1, the interfacial reaction product is : $R(COOH)_2.A_2$;

b. for a molar ratio nearly 1, the extraction system components react in a equimolecular proportion forming : $R(COOH)_2.A$;

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 $[\,R(COOH)_2]_m.A_p$ [6] .

For establishing the extraction mechanism the variation of the reactive extraction degree with dicarboxylic acids initial concentration in aqueous solution has been represented and compared with the theoretical curves corresponding to the proposed mechanisms (Figures 2, 3, 4, 5 and 6 where 1 - experimental values, 2 - theoretical values corresponding to mechanism **a.**, 3 - theoretical values corresponding to mechanism **b.**, 4 - theoretical values corresponding to mechanism **c.**).

As observed, for the proposed experimental conditions, at a value of the molar ratio between dicarboxylic acid and Amberlite LA-2 of 0.8 - 1 the extraction mechanism was **b.** The existed differences between theoretical and

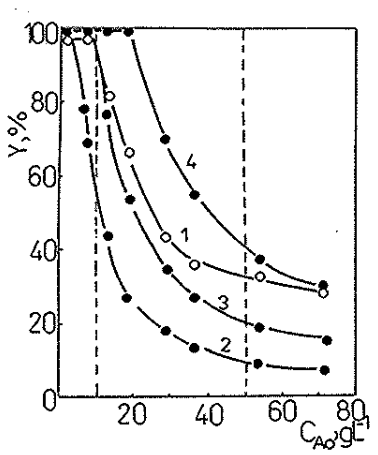

Figure 2. Variation of reactive extraction degree *versus* initial concentration of oxalic acid in aqueous phase.

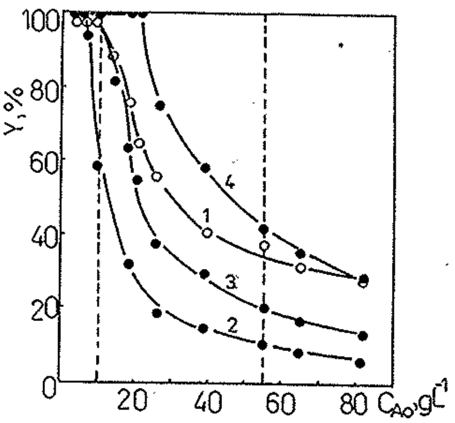

Figure 3. Variation of reactive extraction degree *versus* initial concentration of malonic acid in aqueous phase.

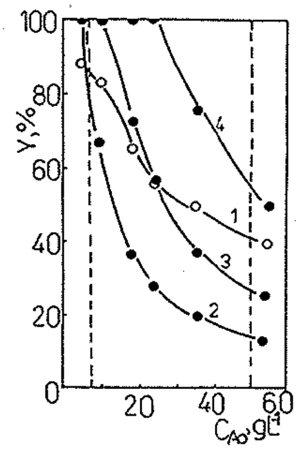

Figure 4. Variation of reactive extraction degree *versus* initial concentration of succinic acid in aqueous phase.

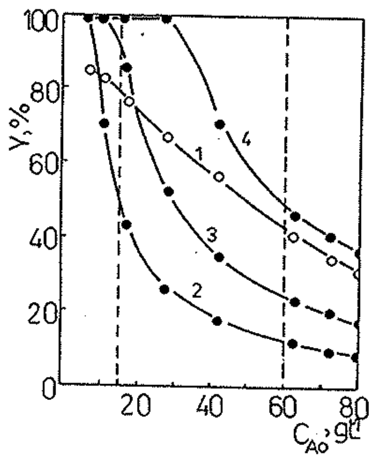

Figure 5. Variation of reactive extraction degree *versus* initial concentration of glutaric acid in aqueous phase.

real extraction degree values are the result both of the variation of acidic constant for the considered acids and of the resistance to the system components diffusion.

At the initial molar ratio values greater than 4.5, the formation of complexes of **c.** type is possible. Adipic acid represents an exception because of his low solubility in aqueous phase and low acidity compared with the other dicarboxylic acids, the reactive extraction mechanism being of **b.** type for all acid concentration range.

Both mechanisms **b.** and **c.** are involved simultaneously in mass transfer process for a molar ratio included between the previous values, as seen from the extraction yield variation.

b. Limiting Steps

The overall reactive extraction process can be determined by two types of resistance : diffusion and/or chemical reaction. For settle the relative importance of one among them the dependence between the transferred solute

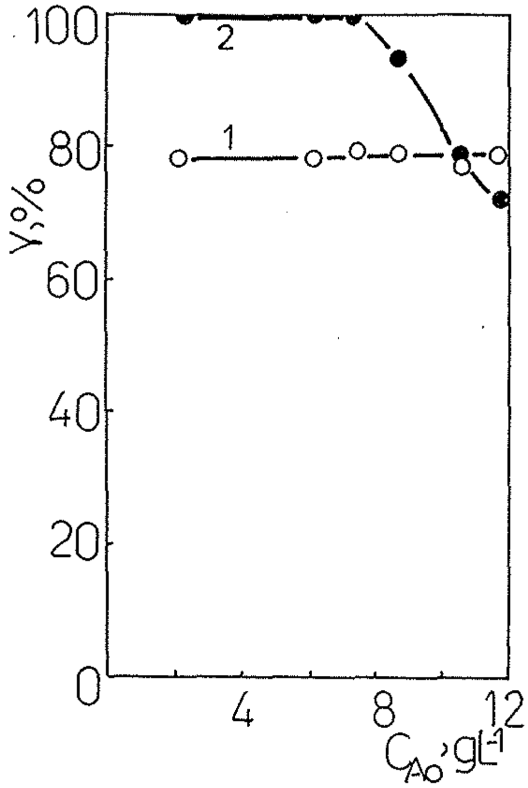

Figure 6. Variation of reactive extraction degree *versus* initial concentration of adipic acid in aqueous phase.

mass flow and the rotation speed has been studied. Thus, for low values of mixing intensity the reactive extraction process is most likely diffusional limited. By increasing the rotation speed of the stirrer, the overall mass transfer process is gradually controlled by the chemical reaction, so that over a certain rotation speed value specific to each dicarboxylic acid the chemical reaction becomes the limiting step.

As seen in Figure 7 the rotation speed range corresponding to the diffusional regime depends on the acidic constant of dicarboxylic acids (the values of the acidity for these acids are given in Table 1 [16]). Over the following rotation speed values the chemical reaction controls the overall extraction process :

- oxalic acid : 1000 rpm;
- malonic acid : 960 rpm;
- succinic acid : 900 rpm;
- glutaric acid : 900 rpm;
- adipic acid : 800 rpm, observing a tendency to reduce the rotation speed range in which the diffusion consists the limiting steps with the decrease in acidic strength. These studies have been carried out for a molar ratio value between dicarboxylic acids and Amberlite LA-2 near to 1, so that the interfacial reaction is :

$$R(COOH)_{2\,(aq)} + \; A_{(o)} \rightleftharpoons R(COOH)_2.A_{(o)}$$

This condition has been used because it offers the possibility to compare the mass transfer behaviour for all acids studied.

c. *Reactive Extraction Kinetic*

Considering a reactive extraction mechanism of **b.** type the expression for reaction rate is :

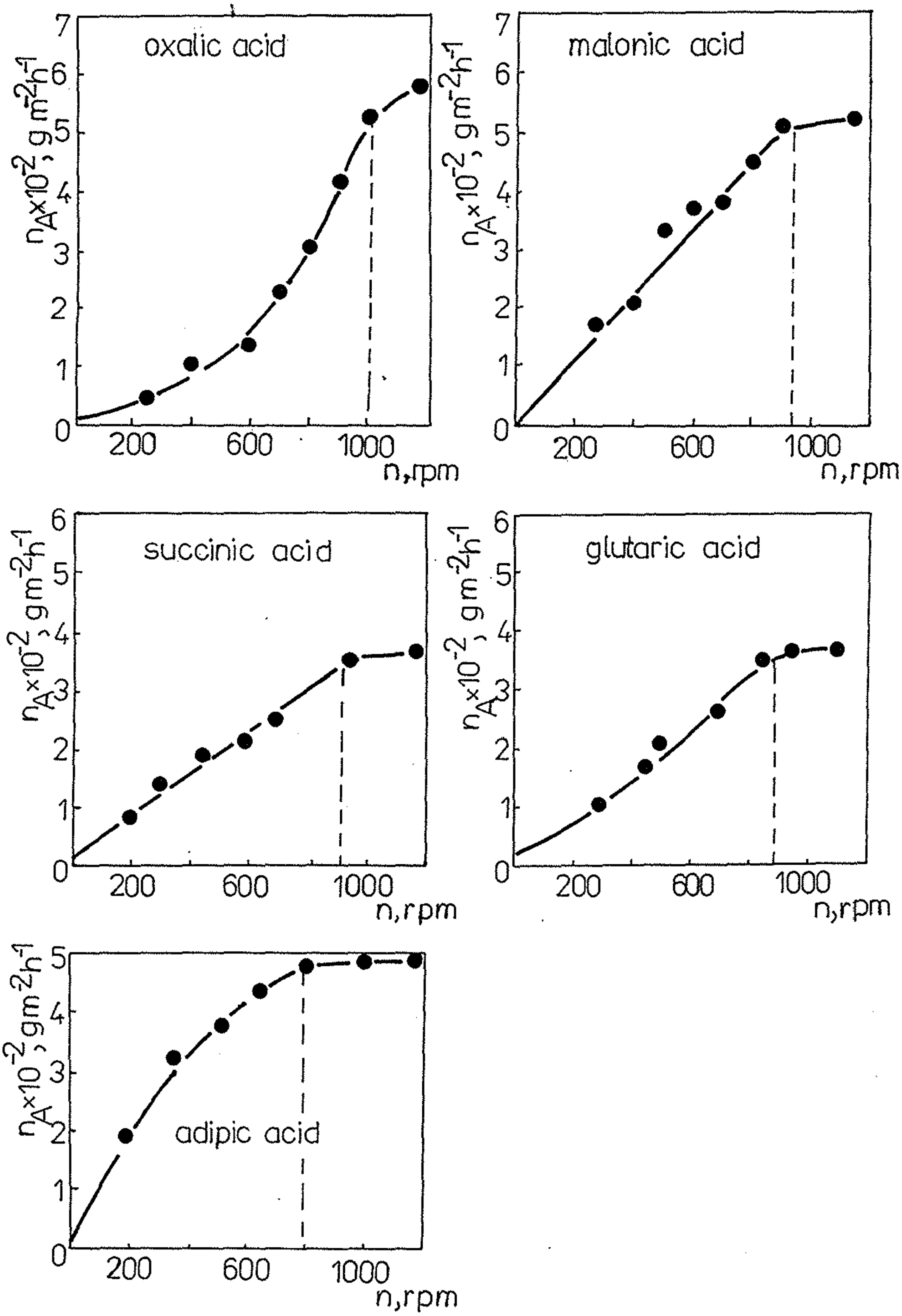

Figure 7. Specific mass flow *versus* rotation speed.

Table 1. Values of the acidic constants for the extracted dicarboxylic acids.

Dicarboxylic acid	k_1	k_2
Oxalic acid	$6.5\ 10^{-2}$	$6.1\ 10^{-5}$
Malonic acid	$1.4\ 10^{-2}$	$8.7\ 10^{-7}$
Succinic acid	$6.9\ 10^{-5}$	$2.8\ 10^{-6}$
Glutaric acid	$4.5\ 10^{-5}$	$3.8\ 10^{-6}$
Adipic acid	$3.7\ 10^{-5}$	$3.9\ 10^{-6}$

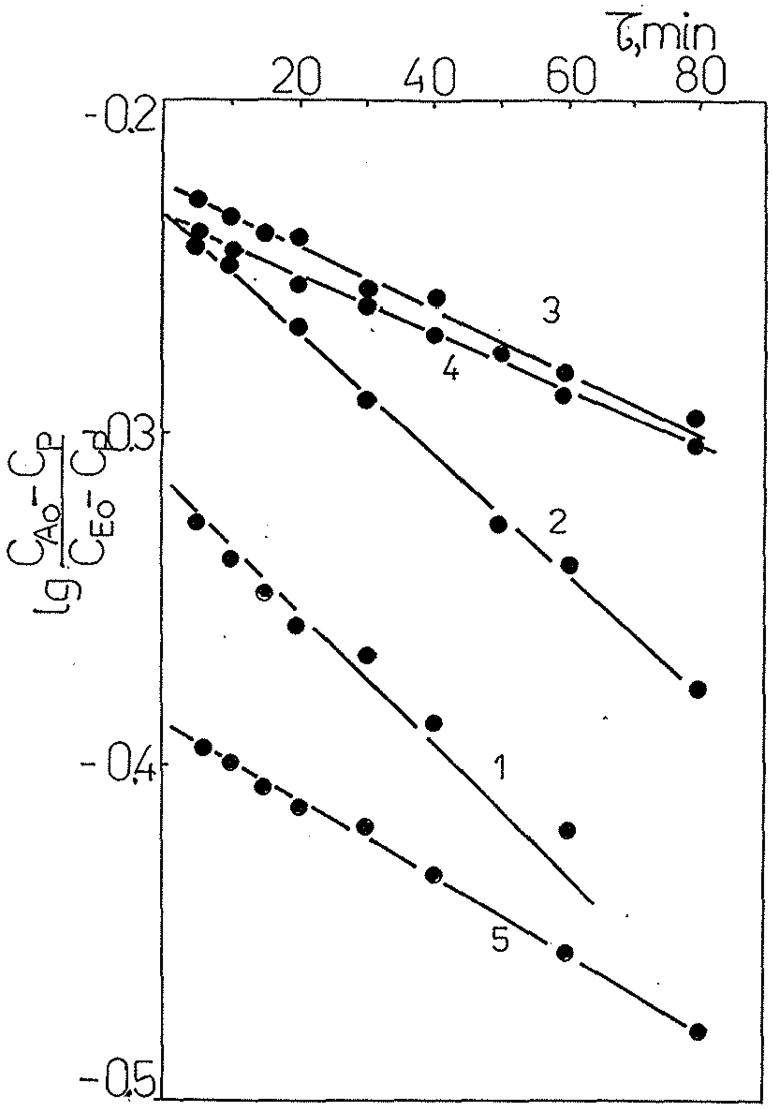

Figure 8. lg $[(C_{Ao} - C_P)/(C_{Eo} - C_P)]$ *versus* extraction time (1 - oxalic acid, 2 - malonic acid, 3 - succinic acid, 4 - glutaric acid, 5 - adipic acid).

Table 2. Experimental values, v_{exp}, and theoretical values, v_{th}, of reaction rate between dicarboxylic acids and Amberlite LA-2.

Dicarboxylic acid	time, min	v_{exp} x10^6, M $L^{-1}s^{-1}$	v_{th} x10^6, M $L^{-1}s^{-1}$	r, %	r_{av}, %
Oxalic acid	5	8.000	7.643	4.46	3.750
	10	7.000	7.130	1.87	
	15	6.671	6.805	2.00	
	20	6.000	6.400	6.67	
Malonic acid	5	8.889	8.844	0.50	2.592
	10	8.000	8.316	3.95	
	20	7.619	7.305	4.12	
	50	4.762	4.896	2.81	
Succinic acid	6	6.000	5.800	3.33	2.24
	10	5.583	5.396	3.35	
	20	4.889	4.927	0.78	
	30	4.670	4.740	1.50	
Glutaric acid	5	6.061	5.913	2.44	2.70
	10	5.555	5.654	1.78	
	20	5.000	5.284	5.69	
	30	4.667	4.709	0.90	
Adipic acid	15	3.000	3.067	2.23	3.95
	30	2.750	2.875	4.54	
	40	2.666	2.688	0.83	
	60	2.220	2.394	7.83	

$$dC_P / d\tau = k_1 (C_{Ao} - C_P) (C_{Eo} - C_P)$$

This study has been carried out for rotation speed value domain corresponding to the kinetic regime. The specific reaction rate was determined by means of the equation obtained by integration of the former one :

$$\lg [(C_{Ao} - C_P)/(C_{Eo} - C_P)] = f (\tau)$$

which represents the straight line equation. The slope of this straight line is : $0.434 (C_{Ao} - C_{Eo}) k_1$ [17] . In Figure 8 are plotted the straight lines for each dicarboxylic acid. Thus, the following values for the specific reaction rate have been obtained :

- oxalic acid : $1.452\text{x}10^{-3}$ M L^{-1}s^{-1};
- malonic acid : $1.419\text{x}10^{-3}$ M L^{-1}s^{-1};
- succinic acid : $8.227\text{x}10^{-4}$ M L^{-1}s^{-1};
- glutaric acid : $8.686\text{x}10^{-4}$ M L^{-1}s^{-1};
- adipic acid : $6.893\text{x}10^{-4}$ M L^{-1}s^{-1}.

The calculated values are confirmed by the experimental values, as resulted from Table 2.

As it was to be expected, the specific reaction rate decreases from oxalic acid to adipic acid. By means of these results and of their acidity, the organic acids studied can be grouped in three categories : oxalic and malonic acids, succinic and glutaric acids, and adipic acid. The specific rate for the reaction between adipic acid and extracting agent is about 2.11 times lower than those corresponding for the reaction between oxalic acid and extracting agent, and about 1.3 times lower than those for glutaric acid.

CONCLUSIONS

These studies on separation of dicarboxylic acids by reactive extraction with Amberlite LA-2 in butyl acetate have indicated the significant influence of the acidic constant variation for the series oxalic acid - adipic acid on extraction degree, on relative importance of the limiting steps and on value of the specific rate of the interfacial chemical reaction between the solute and the extracting agent, even for the similar extraction mechanisms.

List of Symbols

C_A - dicarboxylic acid concentration in aqueous solution;

C_{Ao} - dicarboxylic acid initial concentration in aqueous solution;

C_E - extracting agent concentration in solvent phase;

C_{Eo} - extracting agent initial concentration in solvent phase;

C_P - complex concentration;

k_1 - specific reaction rate;

n - rotation speed;

n_A - specific mass flow of dicarboxylic acid;

r - deviation from experimental values;

r_{av} - average deviation;

τ - extraction time;

Y - reactive extraction degree.

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