

Treatment of Effluents Issued from Agro-Food Industries by Liquid–Liquid Extraction of Malic and Lactic Acids Using Tri-*n*-octylamine and Tri-*n*-butyl Phosphate

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ABSTRACT: The principal objective of this study is to develop new methods for recovery of the acids malic and lactic present in the distilling effluents of the wine industry by solvents. The information about the influence of the factors which govern the thermodynamic equilibrium of all coexistent phases in the aqueous medium of extraction is the essential step. This approach is at the base of the choice of suitable solvent taking into account its selectivity of extraction with respect to the acids lactic and malic. The experimental study showed that the better extents are obtained when the composition of solvent corresponds to 15% (v/v) TOA, 18% (v/v) 1-decanol, and 67% (v/v) *n*-dodecane. The malic percentage of acid extracted is 80%, whereas that of the lactic acid is 53.6%. This last solvent exhibits an excellent extraction efficiency of the malic acid comparatively to lactic acid. The system extractant-diluent (TBP, *n*-dodecane) extracts the lactic acid in a way much more selective from the solution, with a percentage of extraction exceeding 54%. Comparatively to results obtained by the ternary mixture (TOA, 1-decanol, and *n*-dodecane), the separation is more satisfactory using the first system.

■ INTRODUCTION

The liquid–liquid extraction by solvent is a technique largely used in the recovery of the organic acids present in the aqueous solutions.^{1–11} The reactive extraction is used for the recovery and the purification of carboxylic acids with extractants such as the organophosphorus compounds and the aliphatic amines whose molecular weight is very high. The extractants are mixed with various types of diluents which can influence the distribution of compounds between the two phases at equilibrium. In general, the solvent is formed from an extractant and a diluent or from both at the maximum. This diluent plays a significant role when a tertiary amine, characterized by its long carbonaceous chain, is used like an extractant. It is presented in two distinct forms: inert (diluent) and active (modifier).^{3,4,10–13} The inert diluent affects the physical properties of the extraction system in order to activate the extraction process without intervening in the physicochemical mechanism. It contributes to a weak solvation of the interactions product between the various species present in the solution. In solvent, its presence does not have an effect on the product solubility of reaction in the organic phase. However, in this case the extraction is typically physical.^{1–20} The active diluent (modifier) is provided for a functional organic group (ketone, alcohol, etc.) whose favors the solvation of the reaction product while preventing its aggregation within the organic phase. Theoretically, the modifier improves the solubility of the formed complex.^{1,21–31} Without modifier or with low concentrations, the inert diluent is not efficient when we use

the TOA like an extractant, because the polarity of the complex acid-amine reaches its limiting form during separation of the phases or their precipitation. Only the amine has a low capacity of extraction.^{31,32} In the presence of the pure amine or diluted with an inert diluent, the addition of a modifier consequently increases the value of the distribution coefficient.^{12,31} For the experimental results presented in the literature where the extraction equilibrium constants are estimated,^{4,8,19} it was taken into account the various complexes formed between the molecules of acids and the molecules of extractant (complex acid-amine). The composition of solvent depends on the volumetric ratio between the aqueous and organic phases as well as concentration in acid. After interaction of these two phases, the aqueous phase becomes turbid or opaque which is clarified after the addition of distilled water. Such a result is justified by the saturation of the aqueous phase by the product of reaction.³²

For separation of the lactic acid, the ion-exchange resins technique has been the objective of Monteagudo et al.³³ work. However, the high cost of the equipment and the weak capacity of the resins remain an obstacle from an economic point of view. Often, the polar diluents such as alcohols, ethers, and the ketones improve the extractive capacity of solvents. Never-

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theless, they are more soluble in the aqueous phase than the nonpolar compounds. Another class of solvents has been developed. Indeed, the bis 2,4,4-trimethylpentylphosphinic anion (Cyphos IL-104) is an ionic liquid (IL) extractant of HLA with a higher distribution coefficient, while its extraction is carried out by the coordination mechanism. Marták et al.³⁴ showed that with pure Cyphos IL-104 and low acid concentrations, the distribution coefficient values can exceed a value of 40. This extraction causes splitting of reverse micelles with liberation of water from the solvent. The distribution coefficient of Cyphos IL-104 in n-dodecane increases with the temperature when HLA concentration is low to $0.1 \text{ kmol}\cdot\text{m}^{-3}$. In this case, it is advantageous to work at high temperatures in order to increase mass-transfer and rate of reaction. Cyphos IL-104 extracts HLA only in its undissociated form via H-bond coordination according to a reactive extraction in order to form complexes stoichiometrically defined (p, 1, 2) which the structures are $(\text{HLA})_p(\text{IL})(\text{H}_2\text{O})_2$. They note two mechanisms of the extraction into the solvent with Cyphos IL-104: the formation of the reverse micelles and the insertion of water into the hydrated complexes of HLA with IL having two molecules of water in the complex.³⁴

Other similar works on the extraction of the carboxylic acids highlighted the influence of the temperature, the concentration in acid, and the nature of solvent on the equilibrium conditions. Moreover, it was shown that the cyanex 921 has an extractive capacity slightly better than cyanex 923. A thermodynamic calculation of the reaction of extraction was developed.³⁵

In order to separate two acids present simultaneously in the effluent, it is difficult experimentally to choose an important percentage of extraction of the extracted acid. Indeed, a good separation is required so that it be found a compromise between the purity and the distribution coefficient. In certain cases, the increase in the total concentration of the acid present in the aqueous phase leads to the rising of the pH. The presence of impurities, in negligible quantities, does not give the better explication for this result. Only Wardel and King mentioned the effect of extractant and the product of reaction on the capacity of recovery of the acids by the taking into account their physicochemical properties.^{9,32,36–38} The aim of this experimental study is the development of processes of extraction and separation of the lactic and malic acids present in the effluents resulting from agro-food distilleries. Based on the bibliographical analysis relative to the extraction and the physicochemical properties, we retained suitable solvents for the recovery of the carboxylic acids. The analysis is carried out on a synthetic aqueous solutions composed of such carboxylic acids.

MATERIALS AND METHODS

The model aqueous medium was prepared by dissolving L(+)-lactic acid (Sigma–Aldrich) in deionized water (Millipore Milli-Q Water System) without pH adjustment. The lactic acid (85% mass) was distilled under total reflux for 8 h to 10 h for breaking up the dimers. The presence or absence of dimers was controlled by HPLC. We used standard solutions from L(+)-malic acid, pure (99% mass), (Sigma–Aldrich) and pure crystalline L(+)-lactic acid (98% mass) in order to calibrate the HPLC-column.

The third solution is a mixture of carboxylic acids where the concentration is very close to that of the distilleries effluents (malic acid: 2 g/L, lactic acid: 8 g/L).

The tertiary amines tri-n-octylamine (TOA; 98% mass, Acros Organics), tri-iso-octylamine (98% mass TIOA, Sigma Aldrich), and tri-n-butylphosphate (99% mass TBP, Sigma–Aldrich) were used as extractants without further purification. The organic phase (solvent) consisted of the extractant dissolved in the active diluent (modifier) and/or the inert diluent. In this work, the 1-decanol (99% mass) is the active diluent, and the n-dodecane (99% mass, Acros Organics) is used as inactive diluent. The HPLC system was composed respectively from a pump (SpectraPhysics, Model SP8800), autosampler (Spectra Physics SP8875), UV-spectrophotometer (Spectra Physics 100 UV–vis detector: wavelength = 210 nm), integrator (Chromjet SP4400), and column for organic acid analyses (Bio-Rad Aminex Ion Exclusion HPX-87 H) operating at $T = 35 \text{ }^\circ\text{C}$. The mobile phase was 5 mmol/L H_2SO_4 with a flow rate of $0.6 \text{ mL}\cdot\text{min}^{-1}$. The $\text{p}K_a$ values in aqueous solution at $T = 25 \text{ }^\circ\text{C}$ are, for malic acid $\text{p}K_{a2,1} = 3.22$, $\text{p}K_{a2,2} = 4.70$ and for lactic acid $\text{p}K_{a1} = 3.86$ respectively.

The experiments were carried out in 125 mL separators funnels. Equal volumes (20 mL) of aqueous phase containing lactic or malic acids and organic phase were shaken during 20 min at ambient temperature on the digital shaking apparatus IKA HS501 (IKA Labortechnik) with a rotational speed of 280 min^{-1} . This agitation time was sufficient to reach the liquid–liquid equilibrium. After separation of the phases, the volume of each phase was measured using a graduated test tube. The pH of the aqueous phase before and after extraction was measured with a pH-meter equipped with the WTW microprocessor with a temperature compensating probe. The concentrations of lactic and malic acids were determined by high-performance liquid chromatography (HPLC), and the corresponding concentrations in the organic phase were calculated by mass balance.

Under identical conditions, each sample was analyzed three times, and the average value was reported. The analyses were made immediately after separation of phases in order to avoid its possible oxidation by air, evaporation, or eventual bacteriological degradation of the acid. The experimental error was estimated less than 5%. This average value was used in the graphical presentation.

Definition of the Characteristic Parameters. The extraction efficiency is defined by percentage of extraction (E (%)), distribution coefficient (m), purity of lactic acid in the aqueous phase (P_{HLA} (%)), and purity of malic acid in the organic phase $\bar{P}_{\text{H}_2\text{MA}}$ (%).

$$E (\%) = \frac{V_{\text{in}} \cdot C_{\text{in}} - V \cdot C}{V_{\text{in}} \cdot C_{\text{in}}} \times 100 \quad (1)$$

$$m = \frac{\bar{C}}{C} = \frac{V_{\text{in}} \cdot C_{\text{in}} - V \cdot C}{V \cdot C} \quad (2)$$

$$P_{\text{HLA}} (\%) = \frac{C_{\text{HLA}}}{C_{\text{HLA}} + C_{\text{H}_2\text{MA}}} \times 100 \quad (3)$$

and

$$\bar{P}_{\text{H}_2\text{MA}} (\%) = \frac{\bar{C}_{\text{H}_2\text{MA}}}{\bar{C}_{\text{HLA}} + \bar{C}_{\text{H}_2\text{MA}}} \times 100 \quad (4)$$

where

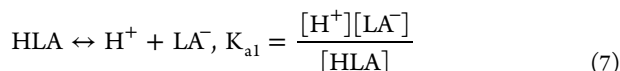
$$C_{\text{HLA}} = [\text{HLA}] + [\text{A}^-] \quad (5)$$

$$C_{H_2MA} = [H_2MA] + [HMA^-] + [MA^{2-}] \quad (6)$$

Equilibrium and Mechanism of Extraction Analysis.

Relating to the law of mass action, the extraction equilibrium of carboxylic acids can be described as a set of equations including the K_a corresponding values. The following reactions take place: 1. the dissociation of the acid in aqueous solution and 2. the formation of reaction product acid-solvent.

– Case no. 1: Dissociation of monocarboxylic acid gives



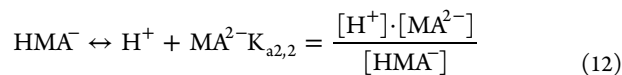
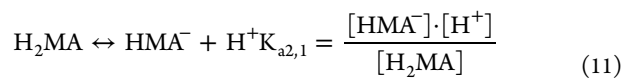
The extraction equilibrium constant of the lactic acid is

$$K_{E1} = \frac{[\overline{E_{n_1}HLA}]}{[HLA] \cdot [\bar{E}]^{n_1}} = \frac{m_{HLA} \cdot (K_{a1} + [H^+])}{[E]^{n_1} \cdot [H^+]} \quad (9)$$

The distribution coefficient of monoacid (m_{HLA}) expresses the ratio between the total concentrations of acid in all of its possible forms in the organic and aqueous phases

$$m_{HLA} = \frac{\bar{C}_{HLA}}{C_{HLA}} = K_{E1} \cdot [\bar{E}]^{n_1} \cdot \frac{[H^+]}{K_{a1} + [H^+]} \quad (10)$$

– Case no. 2: Dissociation of dicarboxylic acid conduces to



$K_{a2,1}$ and $K_{a2,2}$ are the first and second dissociation constants of the diacid and n_2 , the extractant molecules number solvating the molecule of the malic acid. The extraction equilibrium constant of the malic acid is

$$K_{E2} = \frac{[\overline{E_{n_2}H_2MA}]}{[H_2MA] \cdot [\bar{E}]^{n_2}} = \frac{m_{H_2MA} \cdot ([H^+]^2 + K_{a2,1} \cdot [H^+] + K_{a2,2} \cdot K_{a2,1})}{[E]^{n_2} \cdot [H^+]^2} \quad (14)$$

The distribution coefficient (m_{H_2MA}) of the diacid is given by the expression

$$m_{H_2MA} = \frac{\bar{C}_{H_2MA}}{C_{H_2MA}} = \frac{[\overline{E_{n_2}H_2MA}]}{[H_2MA] + [HMA^-] + [MA^{2-}]} = K_{E2} \cdot [\bar{E}]^{n_2} \cdot \frac{[H^+]^2}{[H^+]^2 + K_{a2,1} \cdot [H^+] + K_{a2,1} \cdot K_{a2,2}} \quad (15)$$

If we consider eqs 10 and 15, the ratio of the partition coefficients is

$$\frac{m_{H_2MA}}{m_{HLA}} = \frac{K_{E2}}{K_{E1}} \cdot [\bar{E}]^{n_2 - n_1} \cdot \frac{[H^+] \cdot (K_{a1} + [H^+])}{[H^+]^2 + K_{a2,1} \cdot [H^+] + K_{a2,1} \cdot K_{a2,2}} \quad (16)$$

The choice of the technique of liquid–liquid extraction will depend successfully and entirely on the extraction equilibrium constants (K_{E1}, K_{E2}), composition of the organic phase ($[\bar{E}]$), dissociation constants of the acids, and pH of the aqueous phase. The functional analysis of the ratio of the distribution coefficients, (m_{H_2MA}/m_{HLA}), define an interval of the favorable conditions to their separation.

RESULTS AND DISCUSSION

Solvents Selection. In this step, our objective was to choose the best solvent in order to separate lactic and malic acids. For these preliminary studies, we tested different solvents. The acids were recovered from individual solutions containing lactic or malic acids. With respect to used solutes, three solvents have shown the best selectivity. These solvents are as follows: 1. TOA dissolved in dodecane with 1-decanol as modifier; 2. TIOA dissolved in dodecane with 1-decanol as modifier; and 3. TBP dissolved in dodecane.

For the initial concentrations equal to 8.72 g/L and 2.02 g/L relatively to lactic and malic acids respectively, the obtained results of tests are presented in Table 1.

Table 1. Percentage of Extraction (E (%)) and Ratio between the Distribution Coefficients of Acids for Three Solvents

solvents	E (%)		(m_{H_2MA}/m_{HLA})
	lactic acid	malic acid	
100%(v/v) 1-decanol	10.53	11.77	1.08
100%(v/v) TIOA	39.33	36.62	0.83
100%(v/v) TBP	49.66	46.56	0.88
100%(v/v) TOA	16.22	25.71	1.60
80%(v/v) TBP, 20%(v/v) dodecane	42.49	33.69	0.68
30%(v/v) TOA, 70%(v/v) 1-decanol	87.09	91.86	1.27
30%(v/v) TIOA, 70%(v/v) 1-decanol	85.32	83.13	0.74
10%(v/v) TOA, 70%(v/v) 1-decanol, 20%(v/v) n-dodecane	85.12	95.42	3.65

Based on these tests, we concluded that the first two solvents have a more interesting selectivity with respect to the carboxylic acids because the greatest value of (m_{H_2MA}/m_{HLA}) corresponds to solvents containing TOA, dissolved in n-dodecane with 1-decanol as modifier and TIOA dissolved in n-dodecane with 1-decanol as modifier. Such results are confirmed by other works.^{10,13–25,30–32,36–38}

Determination of the Distribution Coefficients of the Lactic and Malic Acids from the System: TOA, 1- Decanol, n-Dodecane. The determination of the distribution coefficients is carried out starting from synthetic solutions containing the lactic and the malic acids. The influence of the concentrations of the active diluent and the extractant on the values of the distribution coefficients (m) is analyzed. The experiments are carried out for pH aqueous solution ($pH_{HLA} = 2.68$; $pH_{H_2MA} = 2.75$) and for a volumetric ratio in the solvent equal to 1. When we choose the concentrations of amine

(TOA) equal to 10 and 20% (v/v), we investigated the concentration effect in 1-decanol on the distribution coefficient, in a sufficiently large interval. For concentrations in lactic and malic acids, respectively equal to 8.8 g/L and 1.912 g/L, and to TOA concentrations in the organic phase close to 10% (v/v) and 20% (v/v), the results relating to the variation of their distribution coefficients versus the 1-decanol, n-dodecane concentrations are consigned numerically in Table 2 and graphically presented in Figure 1.

Table 2. Influence of the Concentration in 1-Decanol on the Percentage of Extraction^a

volume fraction of 1-decanol	E (%)			E (%)		
	lactic acid	malic acid	E_{H_2MA}/E_{HLA}	lactic acid	malic acid	E_{H_2MA}/E_{HLA}
5	12.46	21.66	1.74	23.83	28.87	1.21
10	23.62	31.44	1.33	33.85	49.54	1.46
20	44.34	73.68	1.66	61.64	84.28	1.36
30	67.30	88.49	1.31	79.40	92.58	1.16
50	80.27	92.03	1.14	85.17	92.61	1.08
70	85.12	95.42	1.12	86.62	92.18	1.06

^aHLA: lactic acid. H₂MA: malic acid.

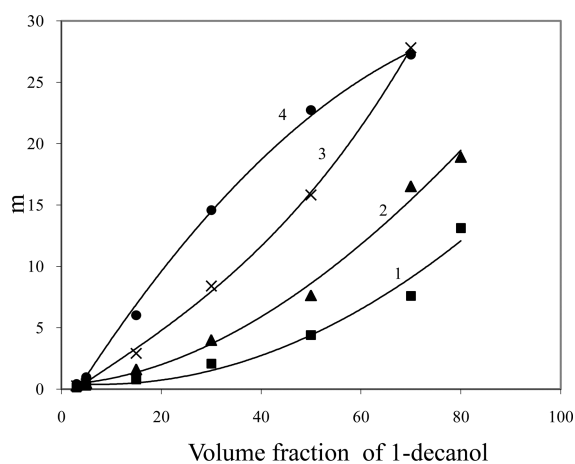


Figure 1. Influence of the 1-decanol concentration on the distribution coefficient of the lactic and malic acids. Curve 1: (■) volume fraction of TOA = 10%, lactic acid. Curve 2: (▲) volume fraction of TOA = 20%, lactic acid. Curve 3: (×) volume fraction of TOA = 10%, malic acid. Curve 4: (●) volume fraction of TOA = 20%, malic acid.

It is necessary to note that the composition of the organic phase in n-dodecane is deduced using an equilibrium balance so that the final percentage is equal to one.

On the physicochemical level and in the presence of TOA, the increasing of the active diluent concentration promotes the solubility of the formed complex from acid and amine. This observation reflects a consequent increasing of the distribution coefficient of the lactic and malic acids. Indeed, we notice that for the lactic acid, the coefficient has doubled its value for a concentration in 1-decanol equal to 70% (v/v) when the concentration of TOA passes from 10% to 20% (v/v). From Figure 1, one notes that this discrepancy is extenuated with the increase in the concentration in 1-decanol. On the other hand, the diacid behavior of the malic acid affects the complex solubility. One can mention that the distribution coefficient changes the concavity when the concentration of TOA passes from 10% to 20% (v/v). So it results from this that the low

concentrations in TOA are favorable for a better distribution. Indeed, the high concentrations in TOA are responsible for the initiation of the second reaction of acid dissociation. Such a phenomenon led to a regression of this coefficient. Taking into account the results presented in Table 2, a compromise between the capacity of extraction of the two acids and the ratio of the extracted percentages (E_{H_2MA}/E_{HLA}) can be elected for a composition of 15% (v/v) in 1-decanol.

Influence of the Concentration in TOA on the Distribution Coefficient. In addition to the concentrations in lactic and malic acids, respectively equal to 8.31 g/L and 1.85 g/L and for a concentration in 1-decanol, equal to that selected above (15% (v/v)), the experimental results presenting the influence of the concentration in extractant on the distribution coefficients of the lactic and malic acids are graphically consigned in Figure 2. It is noted that the increasing in the

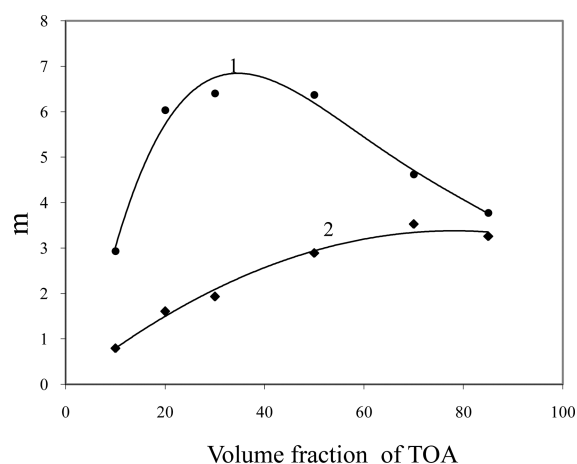


Figure 2. Distribution coefficient of the acids lactic and malic versus the concentration in TOA. Curve 1: (●) malic acid. Curve 2: (■) lactic acid.

amine concentration (TOA) led at a progressive improvement of the distribution coefficient of the lactic acid (curve 2). However, this distribution coefficient increases with the percentage in amine (TOA) in the case of malic acid to establish a maximum for a concentration close to 40% (v/v) of TOA (curve 1). Such a result was amply discussed through many bibliographical references cited on the extraction of the carboxylic acids by a tertiary amine with one diluent.^{12, 24, 37} Taking into account its important solubility in the water and from its basic nature, the increasing in the tertiary amines tri-n-octylamine concentration (TOA) led to a higher pH of the aqueous phase. Consequently, it results in a decelerating of the phenomenon of solute transfer from the aqueous solution toward the organic phase. An exhaustive analysis of the literature relating to the carboxylic acids extraction by an amine and a binary diluent (active and inert) shows that we have few data so that any modeling is quasi impossible in order to study the behavior of the system in aqueous solution. For this reason, we undertook this study where we have detected the existence of a maximum for concentration in TOA, for the malic acid, too close to 40% (v/v). In addition, for the concentrations in lactic and malic acids, respectively equal to 8.45 g/L and 1.89 g/L and with a volumetric ratio (extractant (TOA)/active diluent (1-decanol)) equal to one, the experimental results presenting the influence of the concentration in extractant (TOA) on the distribution coefficients of the lactic and malic acids are given

graphically in Figure 3. For a constant ratio ((extractant (TOA)/active diluents (1-decanol)), we notice that the

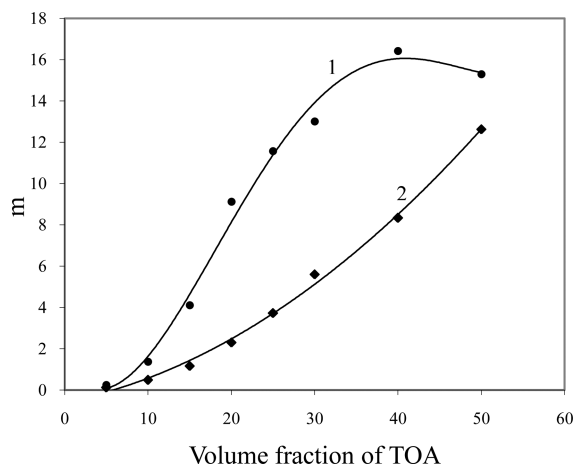


Figure 3. Distribution coefficient of the lactic and malic acids versus to the initial concentration in TOA. Volumetric ratio (extractant (TOA)/diluent active (1-decanol)) equal to 1. Curve 1: (●) malic acid. Curve 2: (■) lactic acid.

increase in their individual concentrations improve the distribution coefficient of the lactic acid (curve 2).

Reporting to the malic acid behavior, we note that the curve trend presented on Figure 2 is, again confirmed, passing by a maximum for a concentration of TOA close to 40% (v/v) (Figure 3, curve 1). It is clear that the composition of dodecane is 20% (v/v). However, the high concentrations in both products (extractant and active diluent) improve the obtaining of the significant percentages in extracted acids. Thus, for any efficiency depollution of the effluents and without worrying about the process selectivity, one can suggest a solvent composition out of about 40% (v/v) in TOA.

Identification of the Optimal Domain of Separation of Recovered Acids. From the point of view processes, the recovery of acids must be followed by separation of the acids existing in effluent. While retaining concentrations initial in lactic and malic acids, respectively equal to 8.45 g/L and 1.89 g/L, the experiences have been released with synthetic solutions in order to find the operating conditions for a better separation of acids. On the basis of purity of the malic acid separated from the organic phase (\bar{P}_{H_2MA} (%)), we determined the optimal conditions versus the solvent concentrations. For a ratio (TOA/1-decanol) equal to one, the experimental results relating to the influence of the concentration in TOA on (\bar{P}_{H_2MA} (%)) and (m_{H_2MA}/m_{HLA}) are graphically presented in Figure 4. Indeed, the more interesting composition of solvent is a compromise between the separation capacity and the purity. The analysis of the two curves in Figure 4, (\bar{P}_{H_2MA} (%)) = f (volume fraction of TOA) and (m_{H_2MA}/m_{HLA}) = f (volume fraction of TOA), shows that the intersection point is close to 15% in volume of TOA, which represents the optimum conditions for separation of the two acids. Beyond, the relative purity of malic acid in the organic phase decreases.

Delimitation of the Optimal Concentrations of Extractant for Separation of the Malic Acid. Knowing that only the complexes formed by interaction between TOA and alcohol contribute to the best extraction and that the chemical equilibrium of the system (aqueous solution of

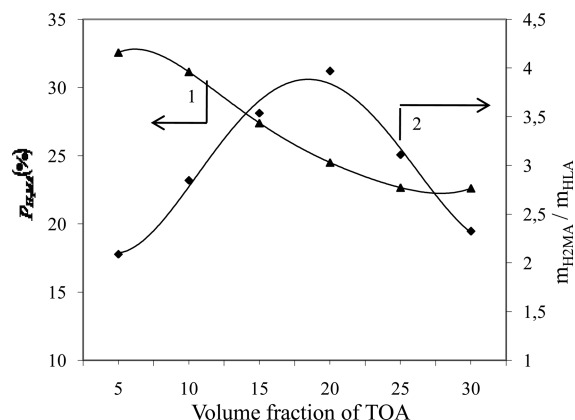


Figure 4. Influence of the concentration in TOA on the ratio of the distribution coefficients and purity of the acid in the organic phase. Volumetric ratio (extractant (TOA)/active diluent (1-decanol)) equal to 1. Curve 1: \bar{P}_{H_2MA} (%). Curve 2: (m_{H_2MA}/m_{HLA}).

carboxylic acid -tertiary amine - binary diluents) strongly depends on the nature of all the components present in the organic phase. From the statistical molecular interactions, it is obvious that the presence of n-dodecane influences negatively on the components number and consequently it reduces the distribution coefficient (m). This is reflected by a regression of the capacity of the acid extraction.

For an initial concentration in malic acid in the aqueous phase, equal to 1.912 g/L, one notes that the curves $m = f$ (volume fraction of 1-decanol) have shapes which change their convexity according to the concentration in TOA (Figure 5).

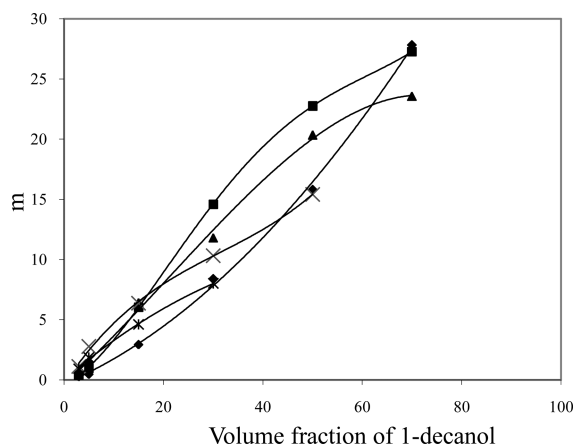


Figure 5. Influence of extractant and modifier (1-decanol) concentration on the distribution coefficient (m).

Indeed, the concentrations equal to 10 and 20% in volume of TOA correspond to the curves enveloping all the curves. This result lets forecast that the optimal conditions of extraction and separation are delimited between these concentrations in TOA. The addition of n-dodecane substantially reduces the viscosity of the solution. Consequently, the mass transfer between the aqueous phase and the organic phase is supported. Such a result corroborates the result obtained fixed in Figure 4.

Extraction of Lactic and Malic Acids by the Tri-n-butylphosphate (TBP), n-Dodecane. To analyze the effect of the extractant nature on the capacity to separate the acid selectively, we used in this part the tri-n-butylphosphate (TBP). Taking into account the fact that solvent (TBP-n-dodecane)

preferentially extracts the carboxylic acids contained in aqueous solution, we study the behavior of each acid taken individually and when they are simultaneously present in a mixture. For initial concentrations in lactic and malic acids equal respectively to 8.45 g/L and 2.14 g/L, the results, expressed in terms of percentages extracted versus volumetric concentration in TBP, are presented in Figure 6. The results highlight an increasing

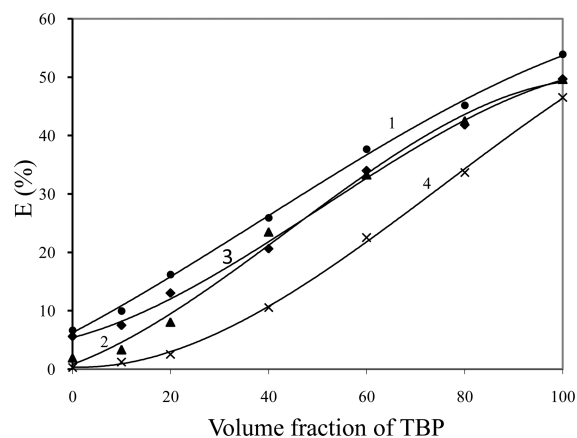


Figure 6. Percentages of lactic and malic acids extracted versus concentration in TBP. Curve 2: (▲) lactic acid solution. Curve 4: (×) malic acid solution. Curve 1: (●) lactic acid in the mixture. Curve 3: (●) malic acid in the mixture.

improvement of the extraction of the two acids with the concentration in TBP. However, this trend is much more marked for the lactic acid taking into account the organophosphorus nature of the TBP (curves 2 and 4). When we analyze the results, relating with the mixture of the two acids, one can advance that the extractant has an extraction capacity slightly selective for the lactic acid (curves 1 and 3). Moreover, for a concentration in the extractant close to 100%, the lactic percentage of extracted acid hardly exceeds 54% whereas that of the malic acid is about 50%. This reveals that the system (TBP, n-dodecane) led to extracts of acids which are found again in the mixture in the extracted organic phase. This result forces to us a solid research in order to determine the best experimental conditions for their separation. However, one notes the synergy phenomenon related to the coexistence of the two acids in the mixture. Indeed, the comparison of curves 1 and 2 establishes clearly that the lactic acid is extracted less if it is taken individually. The presence of the malic acid promotes its extraction considerably. In the case of malic acid, a similar result confirms this assertion.

Determination of the Conditions of Separation of the Extracted Acids in Mixture. In the first step, it is very significant to determine the best composition of the solvent (TOA, 1-decanol, n-dodecane) allowing the extraction of the acids present in the mixture all the while based on the results obtained above, relating to the solutions containing each acid individually taken. For that, one analyzed the influence of the concentration of the active diluent on its extraction capacity knowing that the concentrations are respectively of 7.725 g/L for the lactic acid and 2.150 g/L for the malic acid. For a concentration in TOA, fixed at 15% (v/v), the results of percentages of extracted acids are presented in Figure 7. It arises that the lactic and malic acids are extracted until 80% and 100% for concentrations in n-dodecane included in (0 to 35) %.

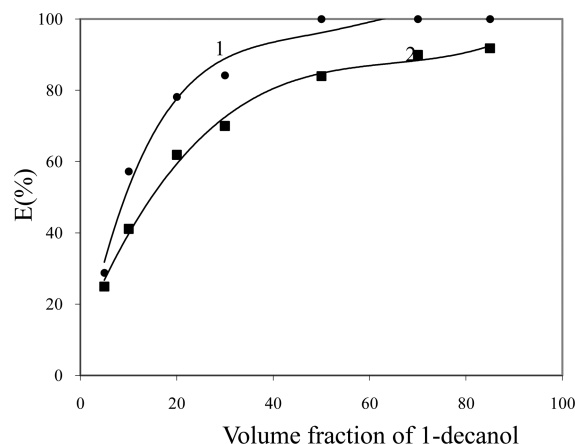


Figure 7. Influence of the 1-decanol concentration on the percentage of the extracted acids from the mixture. Curve 1: (●) malic acid. Curve 2: (■) lactic acid.

The very low n-dodecane concentrations promote the malic acid extraction in a selective way comparatively to the lactic acid. One can advance that the composition of the organic phase has a significant influence on the quantities ratio of extracted acids. Indeed, the experimental study of their separation highlighted the need to add the sufficient quantities of n-dodecane. In objectives to reuse the acids in a pure state, a related process of separation of the two acids is to be set up. Accordingly, the analysis of the best composition of the organic phase allowing their separation led to the curves presented in Figure 8, where purity of the malic acid in the organic phase,

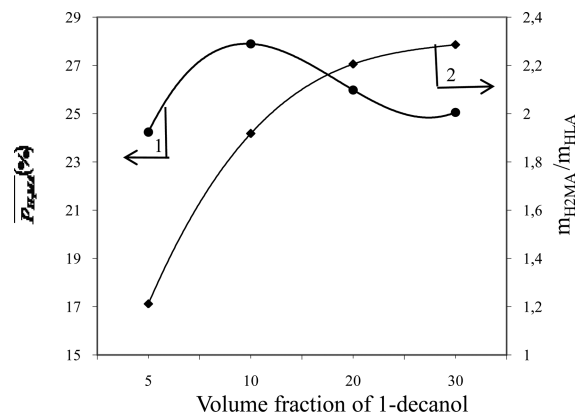


Figure 8. Influence of the 1-decanol concentration on the purity of the malic acid and on the ratio of the distribution coefficients of the acids in the mixture. Volume fraction of TOA = 15%. Curve 1: \bar{P}_{H_2MA} (%). Curve 2: (m_{H_2MA}/m_{HLA}) .

percentage of extract, and the ratio of the distribution coefficients (m_{H_2MA}/m_{HLA}) are traced versus the 1-decanol concentration.

The trend of the curve $(m_{H_2MA}/m_{HLA}) = f$ (volume fraction of 1-decanol) confirms that separation is an increasing function for the malic acid concentration. However, curve \bar{P}_{H_2MA} (%) = f (volume fraction of 1-decanol) is characterized by an irregular shape, in the interval of study, while having a common point with curve $(m_{H_2MA}/m_{HLA}) = f$ (volume fraction of 1-decanol). This point of intersection defines the compromise of separation of the two acids. It coincides with a concentration in 1-decanol

bordering 18% (v/v) and a composition in dodecane equal to 67% (v/v). This result confirms those obtained for the acids extraction when they are taken in an individual state (Figure 4). This composition in solvent (15% (v/v) TOA, 18% (v/v) 1-decanol, 67% (v/v) n-dodecane) is the compromise between extraction efficiency and selectivity of separation, which makes it possible to extract approximately 53.6% for lactic acid and 80% for malic acid.

CONCLUSION

The aim of this study is to valorize the carboxylic acids contained in wastewater from the agro-food processes which become increasingly significant. In order to depollute it and recover these acids in a nonselective way, it was noted that the increasing in the concentration in amine (TOA) causes a progressive improvement of the distribution coefficient of lactic acid. However, this coefficient grows with the percentage in amine (TOA) in the case of the malic acid to present a maximum for a concentration close to 40% (v/v) in TOA with a sufficient quantity in 1-decanol. The analysis of the curves, $\bar{P}_{H_2MA}(\%) = f(\text{volume fraction of TOA})$ and $(m_{H_2MA}/m_{HLA}) = f(\text{volume fraction of TOA})$, shows that a composition of 15% in volume of TOA is the optimum conditions for separation of the two acids. For the malic acid and independently of the concentration in 1-decanol, the curves relating to the volumetric concentrations 10 and 20% in TOA form an envelope which delimits all the other curves relating to the concentrations in TOA. Again, this result constitutes an orientation in the direction of the localization of the optimum conditions of extraction and separation. Moreover, the compromise between the extraction efficiency and the selectivity of separation of the two acids coincides with a content solvent (15% (v/v) TOA, 18% (v/v) 1-decanol, 67% (v/v) n-dodecane) with extraction ratios equal to 53.6% in lactic acid and 80% in malic acid. This result is in perfect coherence with the data referring to the extraction acids taken in an individual state.

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Notes

The authors declare no competing financial interest.

NOMENCLATURE

C = concentration of acid in aqueous phase (g/L)
 \bar{C} = concentration of acid in organic phase (g/L)
 E = pourcentage of extraction
 \bar{E} = extractant in organic solution
 K_{a1} = acidity constant of lactic acid
 $K_{a2,1}$ = first acidity constant of malic acid
 $K_{a2,2}$ = second acidity constant of malic acid
 K_E = extraction equilibrium constant
 m = distribution coefficient
 N = molecules number of extractant
 P = purity of extracted acid in aqueous phase
 \bar{P} = purity of extracted acid in organic phase
 V = volume of aqueous phase (mL)
 \bar{V} = volume of organic phase (mL)
 TOA = tri-n-octylamine
 TIOA = tri-iso-octylamine

TBP = tri-n-butylphosphate

HLA = lactic acid

H₂MA = malic acid

[−] = concentration of the species in aqueous phase

$\bar{[−]}$ = concentration of the species in organic phase

Subscript

1 = lactic acid

2 = malic acid

in = initial

REFERENCES

- (1) Kertes, A. S.; King, C. J. Extraction Chemistry of Fermentation Product Carboxylic Acids. *Biotechnol. Bioeng.* **1986**, *28*, 269.
- (2) Cusack, R. W.; Glatz, D. J. Apply Liquid-Liquid Extraction to Today's Problems. *Chem. Eng.* **1996**, *94*.
- (3) Tamada, J. A.; Kertes, A. S.; King, C. J. Extraction of Carboxylic Acids with Amine Extractants. Equilibria and Law of Mass Action Modelling. *Ind. Eng. Chem. Res.* **1990**, *29*, 1319.
- (4) Prochazka, J.; Heyberger, A.; Bizek, V.; Kousova, M.; Volaufova, E. Amine Extraction of Hydroxycarboxylic Acids. 2. Comparison of Equilibria for Lactic, Malic, and Citric Acids. *Ind. Eng. Chem. Res.* **1994**, *33*, 1565.
- (5) Prochazka, J.; Heyberger, A.; Volaufova, E. Amine Extraction of Hydroxycarboxylic Acids. 3. Effect of Modifiers on Citric acid Extraction. *Ind. Eng. Chem. Res.* **1997**, *36* (7), 2799.
- (6) Sabolova, E.; Schlosser, Š.; Marták, J. Liquid-liquid Equilibria of Butyric Acid in Water + Solvent Systems with Trioctylamine as Extractant. *J. Chem. Eng. Data* **2001**, *46*, 735.
- (7) Kyuchoukov, G.; Marinova, M.; Molinier, J.; Albet, J.; Malmay, G. Extraction of Lactic Acid by Means of a Mixed Extractant. *Ind. Eng. Chem. Res.* **2001**, *23* (40), 5635.
- (8) Bizek, V.; Horacek, J.; Kousova, M. Amine Extraction of Citric Acid: Effect of Diluent. *Chem. Eng. Sci.* **1993**, *48*, 1447.
- (9) Wardell, J. M.; King, C. J. Solvent Equilibria for Extraction of Carboxylic Acids from Water. *J. Chem. Eng. Data* **1978**, *23* (2), 144.
- (10) Flores-Morales, A.; Albet, J.; Kyuchoukov, G.; Malmay, G.; Molinier, J. Influence of Extractant (TBP and TOA), Diluents, and Modifier on Extraction Equilibrium of Monocarboxylic Acids. *J. Chem. Eng. Data* **2003**, *48*, 847.
- (11) Tamada, J. A.; King, C. J. Extraction of Carboxylic Acids with Amine Extractants. 2. Chemical Interactions and Interpretation of Data. *Ind. Eng. Chem. Res.* **1990**, *29* (7), 1327.
- (12) Malmay, G.; Albet, J.; Putranto, A.; Hanine, H.; Molinier, J. Measurement of Partition Coefficients of Carboxylic Acids Between Water and Triisooctylamine Dissolved in Various Diluents. *J. Chem. Eng. Data* **1998**, *43*, 849.
- (13) Kirsch, T.; Ziegenfuss, H.; Maurer, G. Distribution of Citric, Acetic and Oxalic Acids between Water and Organic Solutions of Tri-n-octylamine. *Fluid Phase Equilib.* **1997**, *129*, 235.
- (14) Kirsch, T.; Maurer, G. Distribution of Binary Mixtures of Citric, Acetic and Oxalic Acids between Water and Organic Solutions of Tri-n-octylamine. Part. I. Organic Solvent Toluene. *Fluid Phase Equilib.* **1997**, *131*, 213.
- (15) Matsumoto, M.; Yuba, S.; Kondo, K. Synergistic Extraction of Lactic Acid with Tri-n-octylamine and Tri-n-butylphosphate. *J. Chem. Eng. Jpn.* **1998**, *31* (6), 996.
- (16) Choudhury, B.; Basha, A.; Swaminathan, T. Study of Lactic Acid Extraction with Higher Molecular Weight Aliphatic Amines. *J. Chem. Technol. Biotechnol.* **1998**, *72*, 111.
- (17) Yang, S. T.; White, S. A.; Hsu, S. T. Extraction of Carboxylic Acids with Tertiary and Quaternary Amines: Effect of pH. *Ind. Eng. Chem. Res.* **1991**, *30* (6), 1335.
- (18) Chen, F.; Tanka, H.; Naka, Y.; O'Shima, E. Extraction of Lower Carboxylic Acids from Aqueous Solution by Tri-n-octylamine. *J. Chem. Eng. Jpn.* **1989**, *22* (1), 6.
- (19) Choudhury, B.; Swaminathan, T. Lactic Acid Extraction with Trioctylamine. *Bioproc. Eng.* **1998**, *19*, 317.

(20) Heyberger, A.; Prochazka, J.; Volaufova, E. Extraction of Citric Acid with Tertiary Amine –Third- Phase Formation. *Chem. Eng. Sci.* **1998**, *53*, 515.

(21) Qin, W.; Cao, Y.; Luo, X.; Liu, G.; Dai, Y. Extraction Mechanism and Behavior of Oxalic Acid by Trioctylamine. *Sep. Purif. Technol.* **2001**, *24*, 419.

(22) Roos, M.; Barth, H. J. Extraction of Acetic Acid with Tri-n-octylamine: Physical Properties and Phase Equilibria. *J. Chem. Eng. Data* **2001**, *46* (5), 1198.

(23) Li, Z.; Qin, W.; Dai, Y. Liquid-Liquid Equilibria of Acetic, Propionic, Butyric, and Valeric Acids with Trioctylamine as Extractant. *J. Chem. Eng. Data* **2002**, *47* (4), 843.

(24) Malmay, G.; Vezier, A.; Robert, A.; Mourgues, J.; Conte, T.; Achour, D.; Molinier, J. Recovery of Tartaric and Malic Acids from Dilute Aqueous Effluents by Solvent Extraction Technique. *J. Chem. Technol. Biotechnol.* **1994**, *60*, 67.

(25) Canari, R.; Eyal, A. M. Selectivity in Monocarboxylic Acids Extraction from Their Mixture Solutions Using an Amine-Based Extractant: Effect of pH. *Ind. Eng. Chem. Res.* **2003**, *42* (7), 1301.

(26) Canari, R.; Eyal, A. M. Selectivity in the Extraction of Lactic, Malic, Glutaric, and Maleic Acids from Their Binary Solutions Using an Amine-Based Extractant: Effect of pH. *Ind. Eng. Chem. Res.* **2003**, *42* (7), 1308.

(27) Juang, R. S.; Huang, R. H.; Wu, R. T. Separation of Citric and Lactic Acids in Aqueous Solutions by Solvent Extraction and Liquid Membrane Processes. *J. Membr. Sci.* **1997**, *136*, 89.

(28) Senol, A. Effect of Diluent on Amine Extraction of Acetic Acid: Modeling Considerations. *Ind. Eng. Chem. Res.* **2004**, *43*, 6496.

(29) Prochazka, J.; Heyberger, A.; Volaufova, E. Extraction Equilibrium of Dicarboxylic Acids with Tertiary Amine in Single and Binary Diluents. *Sep. Sci. Technol.* **2004**, *39*, 1073.

(30) Qin, W.; Li, Z.; Dai, Y. Extraction of Monocarboxylic Acids with Trioctylamine: Equilibria and Correlation of Apparent Reactive Equilibrium Constant. *Ind. Eng. Chem. Res.* **2003**, *42*, 6196.

(31) Marinova, M.; Kyuchoukov, G.; Albet, J.; Molinier, J.; Malmay, G. Separation of Tartric and Lactic Acids by Means of Solvent Extraction. *Sep. Purif. Technol.* **2004**, *37*, 199.

(32) Kyuchoukov, G.; Labbaci, A.; Albet, J.; Molinier, J. Simultaneous Influence of Active and Inert Diluents on the Extraction of Lactic Acid by Means of Tri-n-octylamine (TOA) and Triisooctylamine (TIOA). *Ind. Eng. Chem. Res.* **2006**, *45*, 503.

(33) Monteagudo, J.; Aldvero, M. Production of L-Lactic Acid by *Lactobacillus Delbrueckii* in Chemostat Culture Using an Ion Exchange Resins System. *J. Chem. Technol. Biotechnol.* **1999**, *74*, 627.

(34) Marták, J.; Schlosser, Š. Extraction of Lactic Acid by Phosphonium Ionic Liquids. *Sep. Purif. Technol.* **2007**, *57*, 483.

(35) Wisniewski, M.; Pierzchalska, M. Recovery of Carboxylic Acids C1C3 with Organo Phosphine Oxide Solvating Extractants. *J. Chem. Technol. Biotechnol.* **2005**, *80*, 1425.

(36) Labbaci, A.; Kyuchoukov, G.; Albet, J.; Molinier, J. Detailed Investigation of Lactic Acid Extraction with Tributylphosphate Dissolved in Dodecane. *J. Chem. Eng. Data* **2010**, *55*, 228.

(37) Wasewar, K. L.; Shende, D. Z. Equilibrium for the Reactive Extraction of Caproic Acid Using Tri-n-butyl Phosphate in Methyl Isobutyl Ketone and Xylene. *J. Chem. Eng. Data* **2011**, *56*, 3318.

(38) Wasewar, K. L.; Shende, D. Z. Reactive Extraction of Caproic Acid Using Tri-n-butyl Phosphate in Hexanol, Octanol and Decanol. *J. Chem. Eng. Data* **2011**, *56*, 288.