

# Detailed Investigation of Lactic Acid Extraction with Tributylphosphate Dissolved in Dodecane

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The aim of the present study was to study the extraction of lactic acid with tributylphosphate (TBP) dissolved in a diluent (dodecane) over a broad range of acid concentrations and solvent compositions, to determine the apparent equilibrium constants and the number of reacting extractant molecules, and to elucidate the influence of different factors (preliminary washing of organic phase, change of phase volumes, pH at equilibrium, acid concentration) on the extraction of the acid. It was found that the change of phase volumes after extraction should be taken into account for the calculation of different process parameters. The preliminary washing of the extractant does not significantly affect the overall distribution coefficients.

## Introduction

Lactic acid is an important commercial product that has many applications in food, chemical, and pharmaceutical industries. It is a side product of sugar plants and wineries and can also be produced by fermentation or chemical synthesis. The classical way for the recovery of lactic acid is based on the precipitation of calcium lactate; however, this process is technically complex, and additional purification steps are required to obtain commercial-grade lactic acid.<sup>1–3</sup> Ion-exchange resins are also examined for this purpose.<sup>4–8</sup> The high cost of the equipment and the low capacity of the resins limit, however, the applicability of this method. Other attempts to recover lactic acid from the fermentation broth included electrodialysis.<sup>9,10</sup> Among the various methods for lactic acid recovery, solvent extraction with an appropriate solvent has been proposed as a promising alternative to the classical precipitation process.<sup>2</sup>

Different authors have explored the use of strongly basic organic extractants for organic acid extraction from aqueous solutions and have found that organophosphorus compounds and high molecular weight amines are much more effective than conventional solvents.<sup>1–3</sup> As a consequence, many studies have been carried out on the extraction of carboxylic acids with phosphorus-bonded extractants<sup>11,13–16,22–24</sup> and aliphatic amines.<sup>11–13,17–21,23,24</sup>

TBP (tributylphosphate) seems to be an efficient extractant, with regard to the recovery of carboxylic acids. However, it should be diluted in a diluent to decrease its viscosity and density with a view to avoiding excessive energy consumption and improving phase settling in continuous extractors. TBP is a strong Lewis base and interacts chemically with the acids. For evaluation of the distribution coefficient, it is necessary to know the values of the extraction constant and the number of extractant molecules reacting with one molecule of acid. Usually, the mass

action law is applied to their determination, according to the general equation of interaction between the extractant and the extracted substance.

There are many papers where the extraction constant and the number of reacting molecules of extractant are estimated using the mass action law but different values are obtained depending on the solvent composition for the same extractant and organic acid.<sup>2,3,7,10,12–16</sup> The difference between the obtained values of the parameters not only is due to composition changes of the organic phase but also depends on the number of measured factors and the way the experiments are carried out.

The aim of the present study was to study the extraction of lactic acid with tributylphosphate (TBP) dissolved in a diluent (dodecane) over a broad range of acid concentrations and solvent compositions, to determine the extraction constants and the number of reacting extractant molecules, to elucidate the influence of different factors (washing of organic phase, change of phase volume, pH at equilibrium, acid concentration) on the extraction of lactic acid.

## Experimental Section

**Reagents. (a) Extractant.** Tributylphosphate (TBP) with mass fraction ( $\omega = 99\%$ ) was supplied by Acros Organics. It was used either without further purification or after triplicate washing with deionized water.

**(b) Diluent.** Dodecane from Acros Organics ( $\omega = 99\%$ ) was used as an inactive diluent.

**(c) Organic Acid.** Lactic acid ( $\omega = 85\%$ ) was provided by Sigma Aldrich Co. It was distilled under total reflux for (8 to 10) h for breaking up the dimers. The presence or absence of dimers was controlled by high-performance liquid chromatography (HPLC). Pure ( $\omega = 98\%$ ), crystalline L-(+)-lactic acid was used to prepare the standard solutions for the HPLC analyses.

The model aqueous solutions were prepared by dissolving different quantities of lactic acid in deionized water without pH adjustment. Six acid concentrations were prepared between (0.0107 and 1.688) mol·L<sup>-1</sup>.

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The organic phase was prepared by dissolving washed or not washed TBP(I) in dodecane at different volume fractions  $\phi_1 = (10 \text{ to } 80) \%$ . The organic phase containing only TBP or dodecane was also used.

### Experimental Procedure

The experiments were carried out in 125 mL separatory funnels. Equal volumes (20 mL) of the aqueous phase containing lactic acid and organic phase were shaken for 20 min at ambient temperature of  $(20 \pm 1)^\circ\text{C}$  on the shaking machine IKA HS501 digital (IKA Labortechnik) with a frequency of 280 rpm. This mixing time was sufficient to reach the equilibrium. After the phases were separated, the volume of each phase was measured with uncertainties of 0.103 mL. The pH of the aqueous phase before extraction and after phase separation was measured with a WTW microprocessor pH-meter equipped with a temperature-compensating probe. The concentration of lactic acid in the aqueous phase was determined by high-performance liquid chromatography (HPLC). The HPLC system was composed of a pump (Spectra Physics, model SP 8800), autosampler (Spectra Physics, model SP8875), UV-spectrophotometer (Spectra Physics, model 100), UV-vis detector (wavelength of 210 nm), integrator (Chromjet model SP4400), and column for organic acid analyses (Bio-Rad Aminex Ion Exclusion HPX-87 H). The mobile phase was 0.005 M  $\text{H}_2\text{SO}_4$  with a flow rate of  $0.6 \text{ mL}\cdot\text{min}^{-1}$ . Each sample was analyzed in triplicate under identical conditions, and the average value was reported. Each experiment was performed in duplicate or triplicate, under identical experimental conditions. The concentration of lactic acid in the organic phase was calculated from the mass balance according to  $V_{\text{in}}C_{\text{in}} - VC = \bar{V}\bar{C}$ , where  $V$  is the phase volume;  $C$  is the total lactic acid concentration in the aqueous phase; the overbar refers to the organic phase; and the subscript in refers to the initial solution.

The overall distribution coefficient of the acid ( $m$ ) which is the ratio between the total concentrations of acid in all possible forms in the organic and the aqueous phases was calculated according to the following expression

$$m = \frac{\bar{C}}{C} = \frac{C_{\text{in}}V_{\text{in}} - CV}{\bar{V}\bar{C}} \quad (1)$$

The mole fractions of dissociated  $\alpha$  and undissociated  $(1 - \alpha)$  molecules of the acid were determined from the measured pH value and the dissociation constant of lactic acid ( $\text{p}K_a = 3.86$ ;  $K_a = 1.380 \cdot 10^{-4}$ )

$$\alpha = \frac{[\text{A}^-]}{C} = \frac{K_a}{K_a + [\text{H}^+]} \quad (2)$$

$$1 - \alpha = \frac{[\text{HA}]}{C} = \frac{[\text{H}^+]}{K_a + [\text{H}^+]} \quad (3)$$

where  $\text{A}^-$  and  $\text{HA}$  are the anion and undissociated molecules, respectively. The molar concentrations are denoted by square brackets.

Taking into account that only lactic acid is present in the aqueous solution, the theoretical value of pH was calculated from the total acid concentration and the dissociation constant according to

$$[\text{H}^+] = ((-K_a + (K_a^2 + 4K_aC)^{0.5})/2) \quad (4)$$

### Results and Discussion

All experimental data were interpreted on the presumption for an interaction between the extractant ( $E$ ) and the organic acid at the interface according to the following expression



According to the mass action law, the extraction constant ( $K_E$ ) can be expressed as

$$K_E = \frac{[\overline{(E)_n\text{HA}}]}{[\text{HA}][\bar{E}]^n} = \frac{[\overline{(E)_n\text{HA}}]}{C(1 - \alpha)[\bar{E}]^n} = \frac{m_R}{(1 - \alpha)[\bar{E}]^n} \quad (6)$$

where  $m_R = [\overline{(E)_n\text{HA}}]/C$  is the partial distribution coefficient of the interaction product ( $(E)_n\text{HA}$ ) and  $n$  is the number of extractant molecules which interact with one molecule of acid.

The partial distribution coefficient ( $m_d$ ) due to physical extraction by the inert diluent (dodecane) is

$$m_d = \frac{\bar{V}_d[\overline{\text{HA}}]_d}{\bar{V}C} = \frac{\bar{V}_d}{\bar{V}} \cdot \frac{[\overline{\text{HA}}]_d(1 - \alpha)}{[\text{HA}]} = \varphi D_d(1 - \alpha) \quad (7)$$

where  $\varphi = \bar{V}_d/\bar{V}$  is the volume fraction of diluent in the organic phase; the subscript d refers to the diluent; and  $D_d$  is the distribution constant because, according to the Nernst distribution law, the ratio between the concentrations of the transferred solute in coexisting phases at equilibrium is constant if the solute has the same molecular weight in the organic phase as in the aqueous one. Combining eqs 1, 6, and 7 gives after rearrangement

$$\frac{m_R}{1 - \alpha} = \frac{m}{1 - \alpha} - \varphi D_d = K_E[\bar{E}]^n = K_E([\bar{E}]_{\text{in}} - n[\overline{(E)_n\text{HA}}])^n \quad (8)$$

or in logarithmic form

$$\log(m_R/(1 - \alpha)) = \log(m/(1 - \alpha) - \varphi D_d) = \log K_E + n \log[\bar{E}] \quad (9)$$

where

$$[\bar{E}] = [\bar{E}]_{\text{in}} - n[\overline{(E)_n\text{HA}}] \quad (10)$$

The influence of different factors on the determination of the overall distribution coefficient ( $m$ ) was investigated.

**Washed and Not Washed TBP.** Washing of TBP with deionized water in triplicate gave a 10 % increase of its volume. This increase was observed after the first and the second washing but not after the third one. As a result of lactic acid extraction, changes of organic and aqueous phase volumes were not observed, except for the highest initial concentration of lactic acid ( $1.688 \text{ mol}\cdot\text{L}^{-1}$ ) at volume fractions  $\phi_1 = (60, 80, \text{ and } 100) \%$ . This change (equal to increased organic and decreased aqueous phase volume) was (1.25, 2.50, and 3.75) %, respectively.

When the organic phase contained not washed TBP, a change in both volumes was observed. This change depends on the volume fraction of TBP and the initial concentration of lactic acid. It reaches 11.25 % at 100 % TBP and  $1.688 \text{ mol}\cdot\text{L}^{-1}$  initial concentration of lactic acid.

If the extractant (TBP) is not previously washed and the concentration of acid in the organic phase is calculated according to the material balance assuming that there is no change of the phase volumes, a significant relative error appears between the overall distribution coefficient determined in this way and the real one calculated according to eq 1.

As examples, in Table 1 are shown the experimental results at different extractant concentrations when not washed TBP was used and the initial acid concentration was  $0.05380 \text{ mol}\cdot\text{L}^{-1}$ . The difference between the apparent ( $\bar{C}_{\text{app}}$ ) and the real

**Table 1.** Values of the Acid Concentration in the Aqueous Phase ( $C$ ), Real Values of the Acid Concentration in the Organic Phase ( $\bar{C}$ ), Real Values of the Overall Distribution Coefficient ( $m$ ) When the Measured Values of Aqueous ( $V$ ) and Organic ( $\bar{V}$ ) Phase at Equilibrium Are Taken into Account, Values of the Apparent Concentration of Acid in the Organic Phase ( $\bar{C}_{app}$ ), and Apparent Overall Distribution Coefficient ( $m_{app}$ ) and Its Relative Error When the Change of Phase Volumes Is Not Taken into Account at Different Initial Concentrations of Extractant ( $TBP_{in}$ )

$TBP_{in}$ $mol \cdot L^{-1}$	$V$ $cm^3$	$\bar{V}$ $-cm^3$	$C$ $mol \cdot L^{-1}$	$\bar{C} \cdot 10^2$ $mol \cdot L^{-1}$	$\bar{C}_{app} \cdot 10^2$ $mol \cdot L^{-1}$	$m$	$m_{app}$	relative (error %)
0.3387	19.75	20.25	0.05286	0.1585	0.09443	0.0300	0.0179	40.33
0.6775	19.50	20.50	0.05076	0.4208	0.3044	0.0829	0.0600	27.66
1.3549	19.50	20.50	0.04378	1.084	1.002	0.2477	0.2289	7.59
2.0324	19.25	20.75	0.03737	1.719	1.643	0.4599	0.4396	4.40
2.7098	19.00	21.00	0.03108	2.311	2.271	0.7437	0.7309	1.72
3.3872	18.75	21.25	0.02613	2.758	2.767	1.055	1.059	-0.329

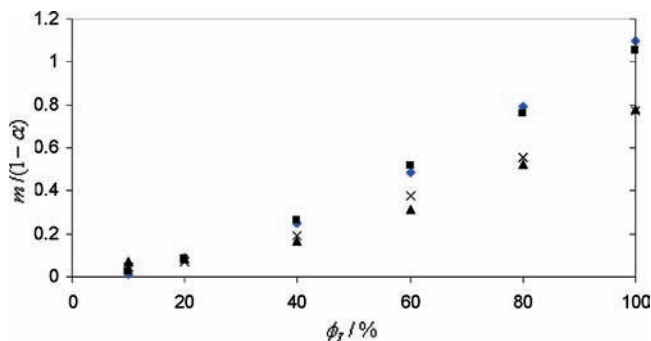
concentration of acid in the organic phase ( $\bar{C}$ ) when the change of volumes after extraction is taken into account is evident. Consequently, it influences the apparent value of the overall distribution coefficient ( $m_{app}$ ), and its relative error can reach high values.

This was the reason to take into account the change of phase volumes for the determination of the real acid concentration and the real concentration of extractant in the organic phase.

Regarding the difference between the overall distribution coefficients using previously washed or not washed extractant, our experiments demonstrated that there is no significant difference between the absolute values of the overall distribution coefficients for both cases, irrespective of the initial acid concentration used, as shown in Figure 1.

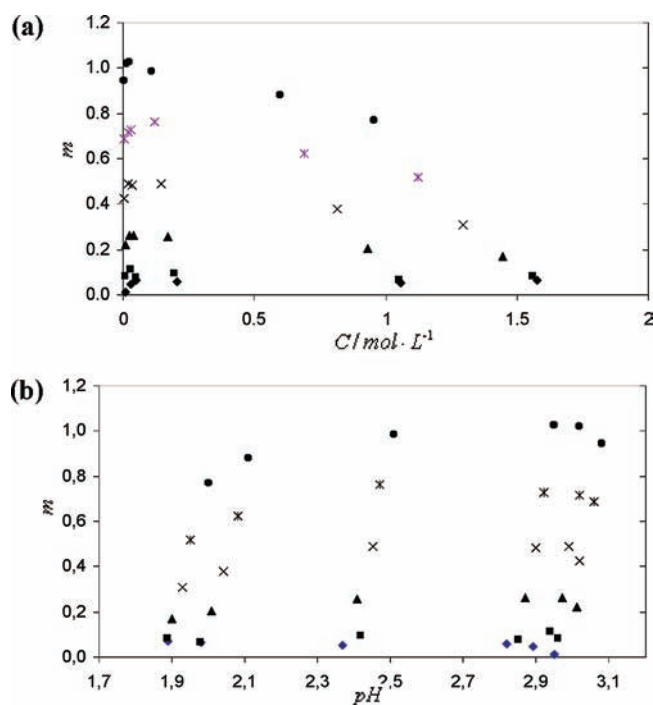
**Influence of Acid Concentration.** The influence of acid concentration on the overall distribution coefficient ( $m$ ) is not evident from eq 8. For the partial distribution coefficient of the interaction product ( $m_R$ ), according to eq 6, the molar fraction of undissociated molecules will increase at higher acid concentrations, and the concentration of free extractant will decrease. The partial distribution coefficient ( $m_d$ ) due to physical extraction will also increase at higher acid concentrations. Obviously, the part of the physical distribution coefficient ( $m_d$ ) depends on the volume ratio between the extractant and the inert diluent. Figure 2a depicts the dependence of the overall distribution coefficient ( $m$ ) on the total acid concentration in the aqueous phase at different volume parts of extractant. It passes through a maximum at the lowest acid concentration, and it is evident for the higher volume part of extractant. Such a dependence was observed by Schlosser et al.<sup>21</sup> for butyric acid and in our previous work for some dicarboxylic acids.<sup>22</sup>

**Influence of pH.** If concentrations in Figure 2a are replaced with the corresponding pH values, the dependence becomes more illustrative (see Figure 2b). At lower pH values, the overall distribution coefficient ( $m$ ) increases with the pH increase. In

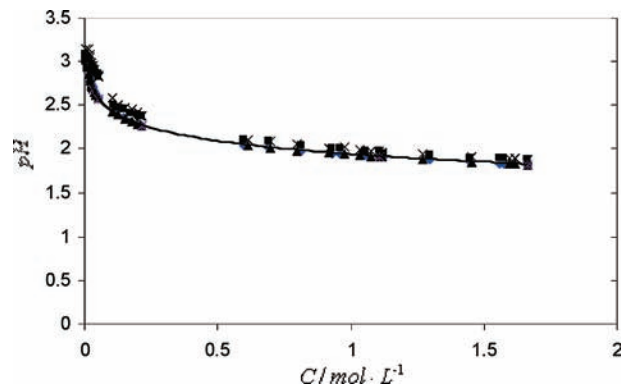


**Figure 1.**  $m/(1 - \alpha)$  vs  $\phi_2$ ; initial concentration of lactic acid,  $0.0107 mol \cdot L^{-1}$ ;  $\blacklozenge$ , previously washed extractant;  $\blacksquare$ , not washed extractant; initial concentration of lactic acid  $1.688 mol \cdot L^{-1}$ ;  $\blacktriangle$ , previously washed extractant;  $\times$ , not washed extractant.

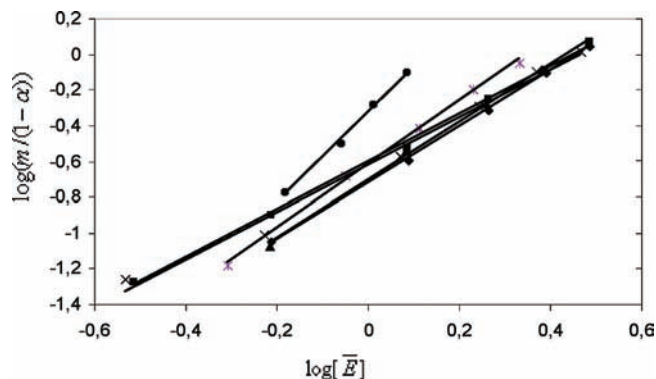
this pH range (high acid concentrations), the influence of the acid concentration on the pH value is not pronounced (see Figure 3), but with the decrease of acid concentration in the aqueous phase, the concentration of free extractant increases. At the same time, owing to the high acid concentration, the acid is present



**Figure 2.** (a) Dependence of the overall distribution coefficient ( $m$ ) on the total acid concentration in the aqueous phase ( $C$ ) at different volume fractions of extractant diluted in dodecane:  $\blacklozenge$ , 10 %;  $\blacksquare$ , 20 %;  $\blacktriangle$ , 40 %;  $\times$ , 60 %;  $*$ , 80 %;  $\bullet$ , 100 %. (b) Dependence of the overall distribution coefficient ( $m$ ) on the measured pH value at different volume fractions of extractant diluted in dodecane:  $\blacklozenge$ , 10 %;  $\blacksquare$ , 20 %;  $\blacktriangle$ , 40 %;  $\times$ , 60 %;  $*$ , 80 %;  $\bullet$ , 100 %.



**Figure 3.** Dependence of pH on the aqueous acid concentration: line, theoretical pH; points, measured values of pH after extraction.



**Figure 4.**  $\log(m/(1 - \alpha))$  vs  $\log[\bar{E}]$  for all studied initial concentrations of lactic acid when washed extractant with its real initial concentration is used for calculation of free extractant concentration ( $n$  is obtained from the slope of the straight line). Initial concentration of lactic acid in  $\text{mol}\cdot\text{L}^{-1}$ :  $\blacklozenge$ , 0.0107;  $\blacksquare$ , 0.0325;  $\blacktriangle$ , 0.0538;  $\times$ , 0.2177;  $*$ , 1.1219;  $\bullet$ , 1.6879.

as undissociated molecules. At higher pH values (lower acid concentrations), the influence of pH on the part of undissociated acid which decreases with the rise of pH is significant and insignificant for the part of the free extractant.

The dependence of pH on the acid concentration is presented in Figure 3. The line depicts the theoretical curve, and the points are the measured values for all experimental data. The points are close to the theoretical curve, the deviations not exceeding  $\pm 0.2$  pH. This means that the concentration of interaction product in the aqueous phase is negligible. The conclusion is valid for the studied case but is not general. In some cases, particularly when amines are used as extractants, the measured pH after extraction is up to one or more pH units higher than the theoretical one.<sup>18,23</sup>

**Determination of the Extraction Constant ( $K_E$ ) and the Number of Extractant Molecules ( $n$ ) Interacting with One Molecule of Acid.** The extraction constant ( $K_E$ ) and the number of extractant molecules ( $n$ ) interacting with one molecule of acid were evaluated according to eq 9. For the determination of these process parameters, the real value of free extractant concentration ( $[\bar{E}]$ ) is required. For this purpose, the number of

extractant molecules ( $n$ ) interacting with one molecule of acid (actually unknown) should be determined. Therefore,  $n$  can be only determined from the slope of the straight line when  $n[(\bar{E})_n\text{HA}] \ll [\bar{E}]_{\text{in}}$ , and  $n[(\bar{E})_n\text{HA}]$  may be neglected. It is very difficult to maintain  $n[(\bar{E})_n\text{HA}] \ll [\bar{E}]_{\text{in}}$  when different concentrations of extractant are used, particularly at high initial concentrations of extracted acid or at high values of the overall distribution coefficient. In this case, the  $n$  used coincides with the slope of the straight line and can be determined by iteration.

Our aim was to compare the obtained  $K_E$  and  $n$  for different cases: (i) use of washed or not washed extractant; (ii) use of apparent or real initial concentration of extractant in the calculations; (iii) considering or not the extraction of organic acid by the diluent. For the determination of  $K_E$  and  $n$ , all data were presented as  $\log(m/(1 - \alpha))$  vs  $\log[\bar{E}]$  or  $\log(m/(1 - \alpha) - \varphi D_d)$  vs  $\log[\bar{E}]$ . As an example, Figure 4 shows  $\log(m/(1 - \alpha))$  vs  $\log[\bar{E}]$  for all studied initial concentrations of lactic acid when prewashed extractant with its real initial concentration was used without taking into account the extraction of organic acid by the diluent. The points for each initial concentration of acid fit into straight lines with different slopes ( $n$ ) in dependence on the acid concentration used. The evaluated  $K_E$  also depends on the acid concentration used.

Generally, at the lowest extractant concentration, for some initial acid concentrations (marked with \* in Tables 2 and 3), the points are situated above or below the straight line, and they are not shown and taken into account. In this way, a coefficient of determination  $R^2 \geq 0.99$  was obtained.

The process parameters ( $K_E$  and  $n$ ) using (i) washed and not washed extractant and (ii) apparent and real initial concentration of extractant in the calculations at different initial acid concentrations in the aqueous phase are shown in Table 2.

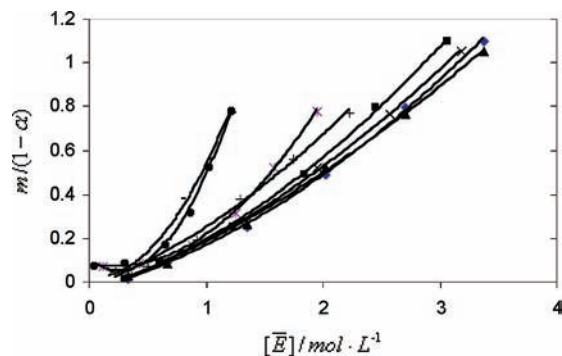
Table 2 illustrates the influence of volume change of the organic phase on the values of  $n$  and  $K_E$  at a given initial acid concentration. When the extractant is previously washed and there is no volume change (see rows 1 to 4 and columns 2 and 6), there is no change of  $n$ . When a volume change takes place (columns 4 and 8 for not washed extractant and rows 5 and 6 (columns 2 and 6) for washed one), the change of  $n$  is

**Table 2.** Real Values of the Extraction Constant for Washed ( $K_E$ ) and Not Washed TBP ( $K_{E(n)}$ ), Apparent Values of the Extraction Constant for Washed ( $K_{E(\text{app})}$ ) and Not Washed TBP ( $K_{E(\text{app}(n))}$ ), Number of Extractant Molecules Interacting with One Molecule of Lactic Acid for Washed ( $n$ ) and Not Washed TBP ( $n_{(n)}$ ), and Apparent Number of Molecules of Extractant Interacting with One Molecule of Lactic Acid for Washed ( $n_{\text{app}}$ ) and Not Washed TBP ( $n_{\text{app}(n)}$ )

$C_{\text{in}} \cdot 10^2$ $\text{mol}\cdot\text{L}^{-1}$	$n$	$K_E \cdot 10$	$n_{(n)}$	$K_{E(n)} \cdot 10$	$n_{\text{app}}$	$K_{E(\text{app})} \cdot 10$	$n_{\text{app}(n)}$	$K_{E(\text{app}(n))} \cdot 10$	
0.069*	1.57	1.888	1.63	1.647	1.57	1.625	1.58	1.593	1
3.250	1.34	2.472	1.26	2.711	1.34	2.175	1.23	2.630	2
5.380*	1.62	1.964	1.64	1.920	1.62	1.680	1.57	1.751	3
21.77	1.32	2.387	1.43	2.234	1.32	2.033	1.35	1.958	4
112.2*	1.78	2.406	1.52	2.868	1.75	1.903	1.37	2.326	5
168.8**	2.37	4.698	2.18	5.267	1.94	2.100	1.56	2.308	6
1	2	3	4	5	6	7	8	9	

**Table 3.** Comparison of the Extraction Constants for Washed ( $K_E$ ) and Not Washed ( $K_{E(n)}$ ) Extractant and the Number of Interacting Molecules of Acid for Washed ( $n$ ) and Not Washed ( $n_{(n)}$ ) Extractant with Their Corresponding Values for Washed ( $K_{E(d)}$ ), ( $n_{(d)}$ ) and Not Washed ( $K_{E(n,d)}$ ), ( $n_{(n,d)}$ ) Extractant When the Extracted Acid by the Diluent Is Taken into Account

$C_{\text{in}} \cdot 10^2$ $\text{mol}\cdot\text{L}^{-1}$	$n$	$K_E \cdot 10$	$n_{(n)}$	$K_{E(n)} \cdot 10$	$n_{(d)}$	$K_{E(d)} \cdot 10$	$n_{(n,d)}$	$K_{E(n,d)} \cdot 10$	
1.069*	1.57	1.888	1.63	1.647	1.66	1.738	1.78	1.586	1
3.250	1.34	2.472	1.26	2.711	1.46	2.246	1.35	2.552	2
5.380*	1.62	1.964	1.64	1.920	1.72	1.810	1.78	1.749	3
21.77	1.32	2.387	1.43	2.234	1.43	2.199	1.49	2.125	4
112.2*	1.78	2.406	1.52	2.868	1.92	2.384	1.45	2.700	5
168.8**	2.37	4.698	2.18	5.267	2.37	4.644	1.98	5.080	6
1	2	3	4	5	6	7	8	9	



**Figure 5.**  $m/(1 - \alpha)$  vs  $[\bar{E}]$ ; initial concentration of lactic acid  $0.0107 \text{ mol}\cdot\text{L}^{-1}$ , previously washed extractant:  $\blacklozenge$ , apparent concentration of TBP used;  $\blacksquare$ , real concentration of TBP used; not washed extractant:  $\blacktriangle$ , apparent concentration of TBP used;  $\times$ , real concentration of TBP used; initial concentration of lactic acid  $1.688 \text{ mol}\cdot\text{L}^{-1}$ , previously washed extractant:  $*$ , apparent concentration of TBP used;  $\bullet$ , real concentration of TBP used; not washed extractant:  $+$ , apparent concentration of TBP used;  $-$ , real concentration of TBP used.

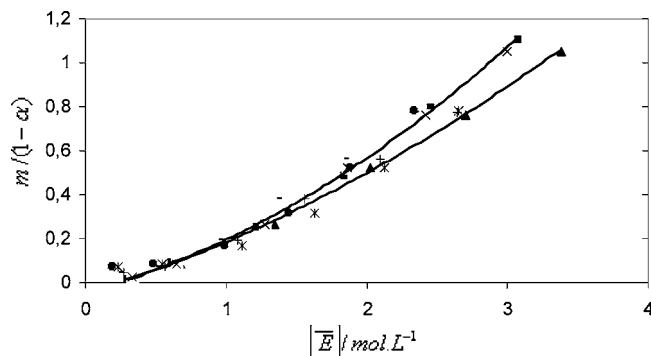
proportional to the volume change. In all cases, when the real extractant concentration is taken into account, the calculated value of  $K_E$  is higher (see columns 3 and 7 for washed and 5 and 9 for not washed extractant) than when the apparent concentration of extractant is used.

To reveal the influence of physical extraction by the diluent on the process parameters ( $K_E$  and  $n$ ), the experimental results were treated according to eq 8 (see columns 6 to 9—real concentration of extractant was used for washed and not washed one).

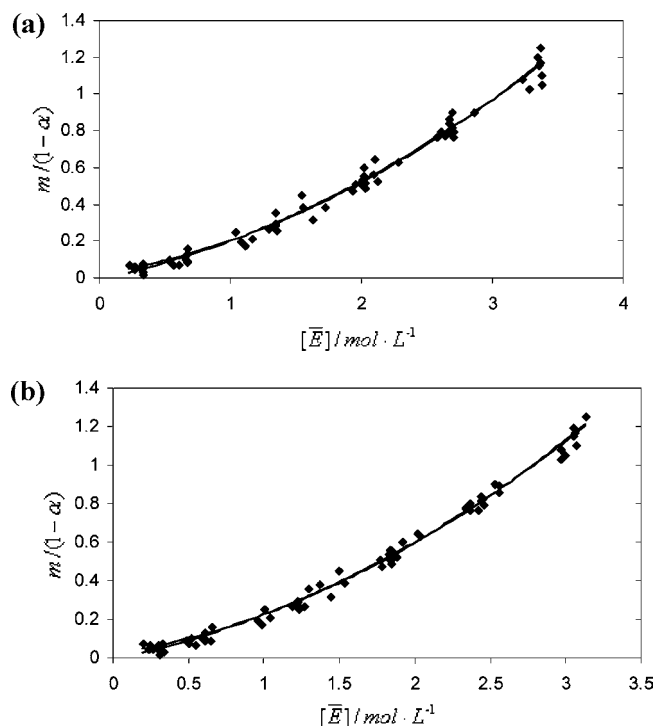
As can be expected, when the physical extraction by the diluent is taken into account,  $K_E$  decreases, but the relative error does not exceed  $-9\%$ , due to the low distribution constant ( $D_d = 0.0136$ ) of lactic acid for the system water and dodecane.

For all studied cases (Tables 2 and 3), the calculated values of  $n$  and  $K_E$  depend on the initial acid concentration. Lactic acid is a monoacid, hence it interacts with one molecule of TBP ( $n = 1$ ). In this case, the data should fit into a straight line according to eq 8, assuming the mechanism proposed by King et al.<sup>18</sup> To check this assumption, all data obtained for the lowest ( $0.01069 \text{ mol}\cdot\text{L}^{-1}$ ) and the highest ( $1.688 \text{ mol}\cdot\text{L}^{-1}$ ) initial acid concentration for all initial extractant concentrations used are presented as  $m/(1 - \alpha)$  vs  $[\bar{E}]$  in Figure 5.

The difference between Figures 1 and 5 is evident. When the initial volume fractions of TBP (washed or not washed) are used in the ordinate (see Figure 1), the dependence of  $m/(1 - \alpha)$  on the initial extractant concentration of all experimental data can be presented by two curves in dependence on the initial acid concentration used. In Figure 5, where the free extractant concentration is used, the number of curves becomes eight in depending on the case (washed or not washed; apparent or real concentration of extractant; lowest or highest initial acid concentration used). What is the reason for this difference? The free extractant concentration was calculated by means of eq 10, where the number of extractant molecules which interact with one molecule of lactic acid ( $n$ ) is taken into account. This number changes as a function of the experimental conditions (see Table 2). If we suppose that one molecule of extractant interacts with one molecule of acid ( $n = 1$ ), all experimental data from Figure 5 could be presented by two curves in dependence on the expression of free extractant concentration—apparent or real. This presentation is shown in Figure 6. It was the reason to present all experimental data for all initial extractant concentrations used independently of initial acid



**Figure 6.**  $m/(1 - \alpha)$  vs  $[\bar{E}]$ ; apparent concentration of TBP used; initial concentrations of lactic acid; previously washed extractant:  $\blacklozenge$ ,  $0.0107 \text{ mol}\cdot\text{L}^{-1}$ ;  $*$ ,  $1.688 \text{ mol}\cdot\text{L}^{-1}$ ; not washed extractant:  $\blacktriangle$ ,  $0.0107 \text{ mol}\cdot\text{L}^{-1}$ ;  $+$ ,  $1.688 \text{ mol}\cdot\text{L}^{-1}$ ; real concentration of TBP used, previously washed extractant:  $\blacksquare$ ,  $0.0107 \text{ mol}\cdot\text{L}^{-1}$ ;  $\bullet$ ,  $1.688 \text{ mol}\cdot\text{L}^{-1}$ ; not washed extractant:  $\times$ ,  $0.0107 \text{ mol}\cdot\text{L}^{-1}$ ;  $-$ ,  $1.688 \text{ mol}\cdot\text{L}^{-1}$ .



**Figure 7.** (a) All experimental points are presented as  $m/(1 - \alpha)$  vs  $[\bar{E}]$  when the apparent free concentration of TBP was used assuming  $n = 1$ . (b) All experimental points are presented as  $m/(1 - \alpha)$  vs  $[\bar{E}]$  when the real free concentration of TBP was used assuming  $n = 1$ .

concentration, washed or not washed extractant, as a function of  $m/(1 - \alpha)$  on the apparent (Figure 7a) or real (Figure 7b) free extractant concentration. In the two latter figures, the points are arranged around a curve corresponding to a second-order equation. The equations which express the curves in Figures 7a and 7b are, respectively:  $m/(1 - \alpha) = 0.0667[\bar{E}]^2 + 0.1156[\bar{E}] + 0.0136$  with coefficient of determination ( $R^2 = 0.9876$ ) and  $m/(1 - \alpha) = 0.0623[\bar{E}]^2 + 0.1226[\bar{E}] + 0.0136$  with coefficient of determination ( $R^2 = 0.9925$ ).

Consequently, it is very important to use the real extractant concentration for the treatment of experimental data.

## Conclusions

This study and the treatment of the experimental data permit the following conclusions.

All experimental results for the extraction of lactic acid by means of TBP dissolved in dodecane at different experimental

conditions can be presented as a dependence of the overall distribution coefficient on the free extractant concentration supposing that one molecule of extractant interacts with one molecule of lactic acid.

The change of phase volume after extraction should be taken into account for the calculation of process parameters. This change influences significantly the real concentration of extractant and the real distribution coefficient.

The use of previously washed or not washed extractant has no significant effect on the extraction.

The measured values of pH after extraction correspond to the theoretical ones, which means that the concentration of the interaction product in the aqueous phase can be neglected.

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