

## Improvement of the Lactic Acid Extraction. Extraction From Aqueous Solutions and Simulated Fermentation Broth by Means of Mixed Extractant and TOA, Partially Loaded with HCl

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Original scientific paper  
Received: March 17, 2004  
Accepted: November 1, 2004

Lactic acid is an important chemical product with wide use in many industrial fields. About a half of world production of lactic acid is made by fermentation of different sugars by means of *Lactobacillus sp.* strains. Two methods for overcoming the problems, arising from the difference in pH optima for extraction and fermentation in the extractive lactic acid fermentation, are proposed. The first method is based on the use of a mixed extractant composed by tri-*n*-octylamine (TOA) and Aliquat 336 (methyltrioctylammomium chloride), dissolved in decanol and dodecane. The use of mixed extractant leads to increase in extraction performance in comparison with individual extractants. The extraction efficiency depends on initial acid concentration, pH and Aliquat/TOA ratio as well. While at 5 g l<sup>-1</sup> lactic acid the distribution coefficient increase with increasing of Aliquat concentration, for 10 and 25 g l<sup>-1</sup> lactic acid the value of distribution coefficient passes through maximum. With increase of acid concentration the position of the maximum shifts to higher TOA concentration. The second method includes the use of tri-*n*-octylamine (TOA) partially converted to amine hydrochloride. This approach leads to increase in the extraction performance in comparison to the extraction with TOA at high pH values. The extraction efficiency depends on initial lactic acid concentration, pH value, and degree of loading with HCl.

### Key words:

Lactic acid, extraction, mixed extractant, modified extractant, trioctylamine, aliquat 336

## Introduction

Lactic acid is a valuable chemical, widely used in pharmaceutical, food, leather, and cosmetic industry. It is also an important source for many chemical syntheses. In the recent years, with the increase in the demand for environmentally friendly materials, the interest of lactic acid production, like a monomer for synthesis of biodegradable polymers, increases. The lactic acid can be manufactured by chemical synthesis (mainly by hydration of lactonitrile synthesized from HCN and acetaldehyde) or by fermentation of different carbohydrates like glucose, lactose or saccharose by various microorganisms of *Lactobacillus* strain.<sup>1–4</sup> One of the problems regarding the lactic acid fermentation is that the process is strongly inhibited by the product. The lactic acid accumulation leads to fast drop of the pH value of the medium on the one

hand and to decreasing of process velocity due to the product inhibition on the other hand. Consequently low substrate conversion, low final concentration of the product, and low conversion have been achieved.

The classical way to overcome this problem is based on neutralization of the broth with Ca(OH)<sub>2</sub>, CaCO<sub>3</sub>, sodium hydroxide or ammonia after separation of the cells. When Ca(OH)<sub>2</sub> is used the additional steps for recovering of the free acid are necessary. The calcium lactate is filtered off and the salt is treated with H<sub>2</sub>SO<sub>4</sub> leading to CaSO<sub>4</sub> and free lactic acid formation.<sup>5</sup> The process of commercially technical grade acid producing is complex and additional purification is needed. As alternative to the traditional recovery process, different techniques have been investigated. These include membrane separation, ion exchange, electrodialysis, aqueous two-phase systems, and liquid-liquid extraction.<sup>6–12</sup> Every of the above mentioned methods have advantages and disadvantages.

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The liquid-liquid extraction in presence of chemical reaction seems to be most promising method for *in situ* separation of lactic acid. This technique permits to keep the product concentration at a low level by continuously removing them from the fermentation broth. By this way the drop in pH value is avoided and the product inhibition is suppressed considerably.

The liquid-liquid extraction is studied extensively in the recent years and different types of extractants have been used.<sup>13–18</sup> Neutral oxygen-containing extractants, such as alcohols, ethers, ketones or esters, are non-specific and give rather low distribution ratios. The extracting capacity of this type of solvent results from the character of the oxygen group attached to a carbon atom, which acts as a Lewis base. When phosphorous-based oxygen containing extractants (tri-*n*-butyl phosphate (TBP), trioctylphosphine oxide (TOPO), etc) have been used, the formation of stable emulsion is observed in many cases. Amine based extractants (primary, secondary and tertiary amines or quaternary ammonium salts) are highly favourable for carboxylic acids extraction. They possess high efficiency and selectivity. The reaction mechanism in this case varies from proton transfer (ion-pair or H-bound formation) to ion exchange. To prevent the third phase formation an inert diluent or a modifier has to be added. The type of used diluent can affect significantly the extraction power of the amine extractants. In general, the polar diluents increase the extraction because they can stabilize the ion-pair formed by hydrogen bonds or by solvation.<sup>19–22</sup> Long chain aliphatic amines are most appropriate for carboxylic acids extraction.<sup>23–27</sup> The primary alkylammonium lactates are either excessively soluble in water or exhibit surface-active properties or both. Lactates of secondary aliphatic amines are more stable and soluble in organic solvents but gel formation can interfere with phase separation. It has been reported that tertiary amines with chain length less than six carbon atoms are poor extractants.<sup>21</sup>

To improve the organic acid extraction different attempts have been made using mixed extractants. *Hong and Hong*<sup>28</sup> have used mixtures of trioctylamine (TOA) and tripropylamine (TPA) in octanol/heptane diluent and have observed a synergistic effect, most pronounced at TOA/TPA ratio 2:8 or 4:6. They have stated that the use of a mixture of a short chain amine with a long chain one prevent a third phase formation. *Matsumoto et al.*,<sup>29</sup> have also observed synergistic effect in extraction system composed from TOA and TBP in hexane. They have also investigated the influence of different diluents and alkylamines.<sup>30</sup> *Juang and Huang*<sup>26</sup> have investigated the influence of di-(2-ethyl-

hexyl)-phosphoric acid (D2EHPA) on the extraction of lactic acid with TOA in xylene and have observed synergistic and antagonistic effects, mainly depending on the concentration ratio D2EHPA to TOA.

*Shierbaum and Vogel*<sup>31</sup> have studied the extraction of lactic acid and acetic acid with dialkylcarboxylic amides and have reported significant enhancement of the system performance in the presence of trialkylamines.

In spite of the extensive research in the lactic acid extraction, two critical problems remain to be solved. The first one is the toxicity of the extractants and solvents against the microorganisms. The second problem is the difference in optimum pH value for extraction and fermentation. Typically, the optimum pH value for the lactic acid production with different microorganisms is in the range 4.5–6.5. It is well known that the extraction of carboxylic acids with tertiary amines or solvating extractants is more appropriate at low pH values, whereas with ion exchange extractants at high pH values.

During the fermentation with accumulation of the lactic acid, the pH value of the system decreases. Applying a solvating extractant or amine for removal of the accumulated acid, the pH value can be maintained to desired level, but as it was mentioned these extractants are not effective at high pH. The use of a quaternary ammonium salt seems to be more appropriate at these conditions. Because of extraction process, the pH values decrease, since the hydrogen ions remain in the system, while the lactate ions are replaced by the corresponding anions of the quaternary ammonium salt (chloride ions in the case of Aliquat 336).

To overcome this problem *Yabannavar and Wang*<sup>32</sup> proposed to realize the simultaneous process of fermentation with immobilized cells and extraction at pH value of 4.2. They have achieved an improvement of the lactic acid production, but at this pH value, neither production of the acid nor the extraction capacity are at their optimum.

*Choudhury and Swaminathan*,<sup>33</sup> have tried to improve the extraction efficiency of TOA at high pH values by using TOA preliminary treated with HCl to form amine hydrochloride. They have reached a four fold increase in the distribution coefficient in comparison with untreated TOA at initial pH 6.0, but the extraction efficiency of treated TOA was less than untreated TOA at a lower pH (2.0).

*Kyuchoukov et al.*,<sup>34</sup> have proposed to use a mixture of an amine (tri-*n*-octylamine) and a quaternary ammonium salt (Aliquat 336) for the lactic acid extraction from the model aqueous solutions. The presumption is that the use of such mixture should

lead to the conditions where the presence of the one extractant should favour the acid extraction by the other one. The proposed method gives certain advantages over the tertiary amines and quaternary ammonium salt, such as better performance in the medium pH region. Probably, the same effect may be achieved when the quaternary ammonium salt is replaced by trioctylamine hydrochloride obtained after reaction of a part of TOA with hydrochloric acid. Having in mind that Aliquat 336 is more toxic to the bacterias than TOA,<sup>35</sup> this should be very important in case of *in situ* extraction of lactic acid.

The purpose of the present work is to study the applicability of the mixed extractant in the case of simulated fermentation broth and to evaluate the influence of different factors, such as pH, acid concentration, and volume ratio of the extractants. Another aim is to investigate the lactic acid extraction from aqueous solutions and from synthetic fermentation broth by means of tri-*n*-octylamine partially converted to amine hydrochloride with HCl. The working hypothesis is that the part of TOA converted to hydrochloride should extract the acid by ion-exchange mechanism and the extractant should act as a mixed one.

## Materials and methods

The 90 % L-(+)-lactic acid (Acros Organics, France) was used for the extraction studies. Because of the presence of dimers of the acid under these conditions (about 25 % of total concentration), ten fold diluted solution was boiled under reflux 8–10 h for dimer hydrolysis. The presence or absence of dimers was controlled by HPLC. The resulting solutions were used for model medium preparation. Pure (98 %) crystalline L-(+)-lactic acid (Sigma, Germany) was used as a standard for HPLC analyses.

As extractants, a tertiary amine tri-*n*-octylamine (TOA) and a quaternary ammonium salt Aliquat 336 (methyltrioctylammoniumchloride), both produced by Acros Organics, were used. The organic phase was composed from extractant ( $\varphi = 30$  %) dissolved in dodecane (50 %) and *n*-decanol (20 %). In some experiments TOA was partially or fully converted to amine hydrochloride by pretreatment with aqueous solutions of HCl (from 0.05 mol l<sup>-1</sup> to 1 mol l<sup>-1</sup>). Stock solutions with desired HCl concentrations were prepared from 1 mol l<sup>-1</sup> volumetric standard solution of HCl (Sigma, Germany). When mixed extractant (TOA + Aliquat 336) was used the ratio between TOA and Aliquat varied from 1:4 to 4:1, respectively.

The experiments were carried out in 125 ml separatory funnels. Equal volumes (25 ml) of aqueous phase containing lactic acid and organic phase

were shaken for 15 min at ambient temperature on the shaking machine IKA HS501 Digital (IKA Labortechnik, Germany). Our preliminary experiments showed that maximum 5 min were sufficient time for attaining the equilibrium. After phases' separation, the volume of the phases, the pH value of the aqueous phase, and the chloride ion concentration were measured. The lactic acid concentrations of the aqueous phase were determined by HPLC and the corresponding concentrations in the organic phase were calculated by mass balance. When needed the initial pH value of the aqueous solution was adjusted with solutions of NaOH and lactic acid with appropriated concentrations. The pre-treatment of TOA with HCl was carried out in the same way as extraction.

The HPLC system was composed from pump, autosampler, UV-detector (Spectra Physics, USA) and integrator (Hewlett Packard, USA). The used column was Aminex HPX-87H (Bio-Rad, USA). As mobile phase 5.0 mmol l<sup>-1</sup> solution of H<sub>2</sub>SO<sub>4</sub> was used at flow rate 0.6 ml min<sup>-1</sup>.

The chloride ion concentrations were determined by means of an ion-selective electrode and Meter Lab (Radiometer Analytical, France) M 240 pH/ion meter. In case of TOA pre-treatment with HCl, the measurements of chloride ions after loading showed that more than 98 % of initial HCl was extracted.

In order to investigate the lactic acid extraction from quasi-real systems, the extraction was realized from solutions containing all components of the fermentation broth (lactose, lactic acid, salts, peptone and yeast extract) except bacteria. The initial pH values of solutions were between 4.5 and 5.8.

Some preliminary tests showed that peptone, yeast extract and lactose do not affect the lactic acid extraction. Choudhury *et al.*,<sup>25</sup> report similar results for glucose and yeast extract and San-Martin and *al.*,<sup>36</sup> for lactose. The total concentration of micro-components in the broth (FeSO<sub>4</sub>, MnSO<sub>4</sub> and MgSO<sub>4</sub>) is very low (less than 1.5 mmol l<sup>-1</sup>) to have significant effect on the extraction. It was decided to continue with solutions containing lactic acid, lactose, sodium acetate, and mono- and di-hydrogen potassium phosphates.

## Results and discussion

### Extraction with mixed extractant

As it was mentioned, a possibility to overcome the problem, due to difference in optimum pH values for extraction with tertiary amine or quaternary ammonium salt and fermentation, is the use a mixture of extractants. Kychoukov *et al.*,<sup>34</sup> have dem-

onstrated the applicability of this idea in case of lactic acid extraction from aqueous solutions at enhanced pH values with system, composed from 15 % TOA, 15 % Aliquat 336 and 70 % decanol. Having in mind that the final goal is to realize an *in situ* extraction of lactic acid from fermentation broth and considering the higher toxicity of decanol toward bacteria compared to dodecane we have decided to decrease the content of decanol to the lower level preventing the third phase formation. The investigated extraction system was composed from  $\varphi = 30\%$ , extractant, 20 % decanol and 50 % dodecane.

The investigation has been started with comparison of extraction performance of systems composed from 15 % TOA, 10 % decanol and 75 % dodecane; 15 % Aliquat, 10 % decanol and 75 % dodecane; 15 % TOA, 15 % Aliquat, 20 % decanol and 50 % dodecane, as well as 30 % TOA (or Aliquat) 20 % decanol and 50 % dodecane. The initial solutions were with lactic acid concentration of  $10 \text{ g l}^{-1}$  with natural pH ( $\sim 2.4$ ) or pH adjusted to 6.0 with  $4 \text{ mol l}^{-1}$  NaOH solution. From the results presented in Figure 1, the better performance of the mixed extractant is clearly seen. The obtained distribution coefficient in case of mixed extractant is higher than these for the individual components at both pH values. Even there is a synergistic effect – the distribution coefficient of the mixed extractant is greater than the sum of distribution coefficients of the two individual components for each pH value. The distribution coefficient obtained with aid of the mixed extractant measures up to 75 – 80 % from the value obtained with 30 % concentration of better extractant for each pH value (TOA at pH 2.4 and Aliquat at pH 6.0). The distribution coefficient ( $K$ ) for a monoacid expresses the ratio of the total concentration of the acid, in all its possible forms in the organic and the aqueous phases.

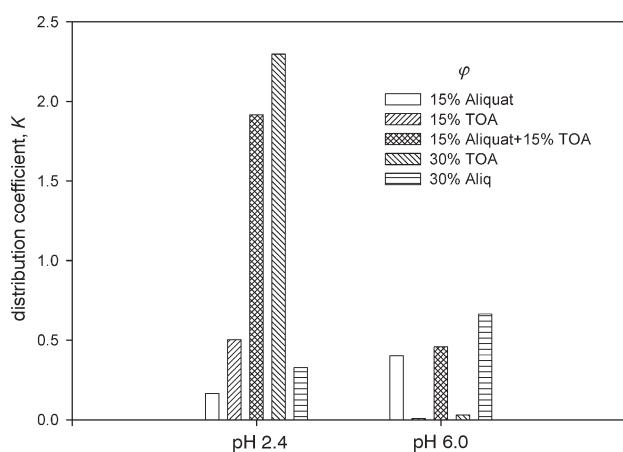


Fig. 1 – Extraction of lactic acid ( $10 \text{ g l}^{-1}$ ) from aqueous solutions at pH 2.4 and pH 6.0 with TOA, Aliquat 336 and mixed extractant. Composition of the organic phase –  $\varphi = 30\%$  extractant,  $\varphi = 20\%$  decanol and  $\varphi = 50\%$  dodecane.

The fermentation broth for lactic acid production from lactose with *Lactobacillus casei* strain contains acetate ions in mass concentration  $10 \text{ g l}^{-1}$  (Beschkov et al.,<sup>9</sup>). There is no information whether acetate is consumed during fermentation or it is used only for enhancement of buffer capacity of the broth. A test for influence of acetate ions on the extraction of lactic acid from simulated fermentation broth was made with mixed extractant composed from 15 % Aliquat and 15 % TOA, and simulated fermentation broth solutions containing  $10 \text{ g l}^{-1}$  lactic acid in the presence and absence of acetate ions. The results presented in Figure 2 demonstrate that the presence of acetate decreases the distribution coefficient in entire investigated pH region from 4.5 to 6.5. Providing that acetate ions are consumed during fermentation, it should enhanced lactic acid extraction. Otherwise, additional experiments are needed to determine the role of the acetate in the fermentation process. In contrast, with fermentation broth with acetate ions, where the final pH is greater than initial with 0.02 to 0.2 pH unit, when one without acetate is used, the final pH after extraction is increased with 0.12 to 0.55 pH units.

In order to determine best ratio between amine and quaternary ammonium salt the experiments have been made with simulated fermentation broth containing 5, 10 and  $25 \text{ g l}^{-1}$  lactic acid (initial pH 4.80, 4.22 and 3.58, respectively). The extraction system was composed of 30 % TOA or Aliquat and 30 % mixed extractant with Aliquat/TOA ratio 1 : 4 (6 %/24 %); 2 : 3 (12 %/18 %); 1 : 1 (15 %/15 %); 3 : 2 (18 %/12 %) and 4 : 1 (24 %/6 %), 20 % decanol and 50 % dodecane.

In case of  $5 \text{ g l}^{-1}$  acid mass concentration, the distribution coefficient increases with increasing of Aliquat's concentration (Figure 3). For  $10 \text{ g l}^{-1}$  the value of the distribution coefficient also increase up

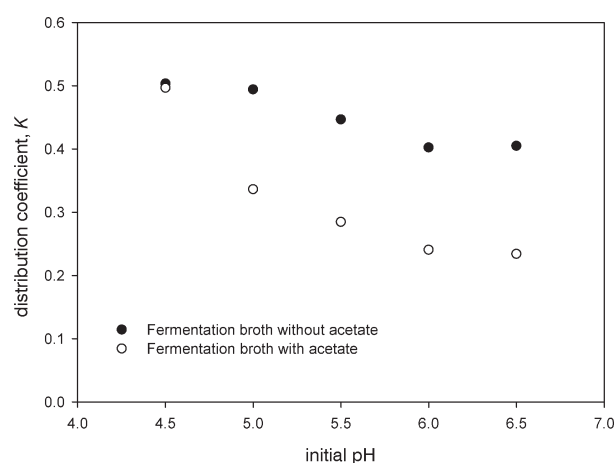


Fig. 2 – Influence of the acetate ions ( $10 \text{ g l}^{-1}$ ) on the extraction of lactic acid (initial concentration  $10 \text{ g l}^{-1}$ ) from simulated fermentation broth with mixed extractant.  $\varphi = 15\%$  TOA,  $\varphi = 15\%$  Aliquat 336,  $\varphi = 20\%$  decanol,  $\varphi = 50\%$  dodecane.

to ratio 4 : 1 (24 %/6 %), but it is lower for pure Aliquat. Finally, for 25 g l<sup>-1</sup> acid concentration, the distribution coefficient starts to decrease from ratio 3 : 2 (18 %/12 %). An interesting fact is that at volume ratio of  $\Psi_{\text{Aliquat/TOA}} = 1 : 4$  (6 %/24 %) and 2 : 3 (12 %/18 %) the distribution coefficient ( $K$ ) for 25 g l<sup>-1</sup> lactic acid is greater than at 5 and 10 g l<sup>-1</sup>, respectively. This probably means a change of extraction mechanism and supplementary investigations are necessary for its elucidation.

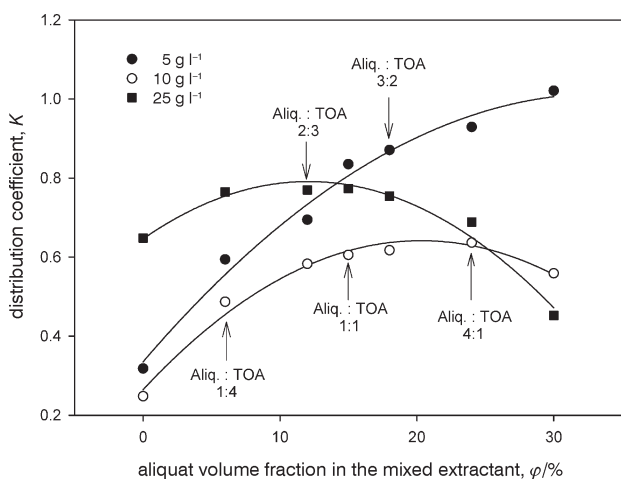


Fig. 3 – Extraction of lactic acid from a simulated fermentation broth by mixed extractant: influence of acid mass concentration (5, 10 and 25 g l<sup>-1</sup>) and mixed extractant composition. TOA volumen fraction  $x$  – %; Aliquat volume fraction –  $30 - x$  %. Initial pH values – 4.8 for 5 g l<sup>-1</sup>; 4.22 for 10 g l<sup>-1</sup> and 3.58 for 25 g l<sup>-1</sup> lactic acid.

It is well known that Aliquat is more appropriate extractant for removal of organic acids at higher pH value, where the acid is almost fully dissociated. That is why in the next experiments the quantity of Aliquat exceeds this of TOA.

In order to investigate the influence of pH on the extraction of lactic acid with mixed extractant, experiments for extraction with synthetic fermentation broth containing 10 g l<sup>-1</sup> lactic acid with ratio  $\Psi_{\text{Aliquat/TOA}} = 1 : 1$  (15 %/15 %); 2 : 1 (20 %/10 %); 3 : 1 (22.5 %/7.5 %) and 4 : 1 (24 %/6 %) were performed at initial pH value from 4.5 to 6.5. The results of this study presented in Figure 4 show that the distribution coefficient decreases with increasing of equilibrium (or initial) pH value. The decrease is most pronounced for the ratio 1 : 1 (15 %/15 %) and best results are obtained with ratio 3 : 1 (22.5 %/7.5 %). In all cases, the equilibrium pH values are higher than initial ones. The difference is between 0.02 and 0.2 pH units, depending on initial pH and Aliquat/TOA ratio (Figure 5). This is very promising for carrying out *in situ* extraction, because maintaining the constant pH value is necessary for successful realization of the fermentation.

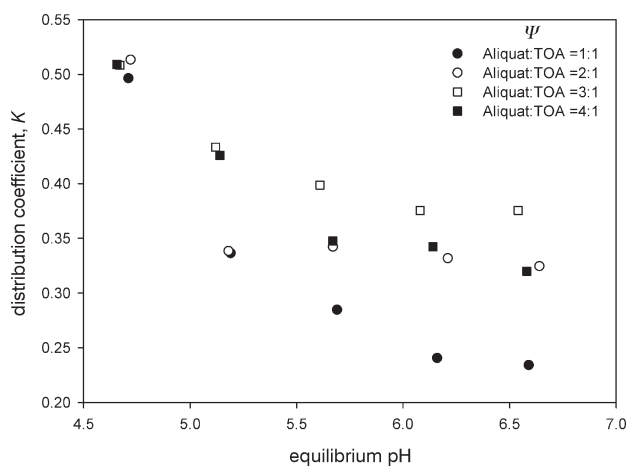


Fig. 4 – Extraction of lactic acid from a simulated fermentation broth by mixed extractant: influence of equilibrium pH value and Aliquat 336 to TOA ratio. Composition of the organic phase –  $\varphi = 30$  % extractant,  $\varphi = 20$  % decanol and  $\varphi = 50$  % dodecane.

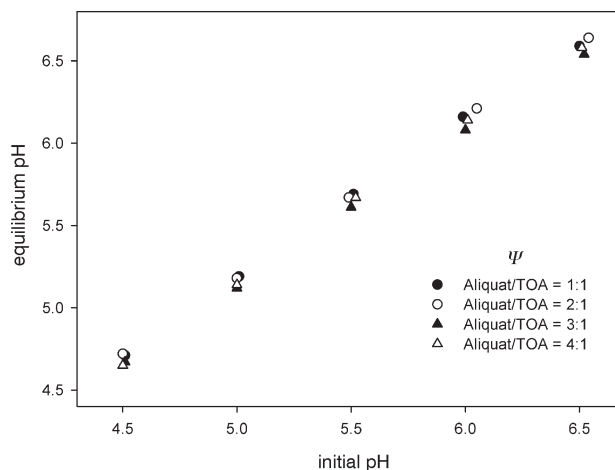


Fig. 5 – Relationship between initial and equilibrium pH values. Lactic acid concentration 10 g l<sup>-1</sup>, initial pH 4.5–6.5. Composition of the organic phase –  $\varphi = 30$  % extractant,  $\varphi = 20$  % decanol and  $\varphi = 50$  % dodecane.

The better performance of mixed extractant in the lactic acid extraction led us to the idea of using TOA, partially loaded with hydrochloric acid for extraction. In this case, the part of amine converted to amine hydrochloride should extract the acid by ion-exchange mechanism and a similar effect, as in the case of mixed extractant, is expected.

### Extraction with TOA partially loaded with HCl

#### Extraction of lactic acid from aqueous solutions with TOA partially loaded with HCl

As it was mentioned, the main disadvantage in organic acid extraction with TOA is the decrease of

distribution coefficient with increase of pH. In the case of lactic acid extraction from fermentation broth, pH value has to be maintained in the range 4.5 – 6.5, because these are the limits in which the fermentation is realizable. When TOA is partially converted to amine hydrochloride, the pH value will decrease during extraction. In this manner the value of the distribution coefficient will increase.

In order to verify this hypothesis we investigated the lactic acid ( $10 \text{ g l}^{-1}$ ) extraction with HCl treated TOA at elevated initial pH value (4.0 – 6.5). In this case, contrary to the extraction with untreated TOA, the equilibrium pH values were lower than the initial ones (see Table 1). From the results presented in Figure 6, it is obvious that the distribution coefficient ( $K$ ) depends on initial pH and degree of TOA loading with HCl. Maximal values of the distribution coefficient were obtained in case of initial pH 4.0 and TOA loaded with  $0.3 \text{ mol l}^{-1}$  HCl, but equilibrium pH is out of the optimum limits for fermentation. Having in mind, that distribution coefficient depends also on the pH value (i.e. the initial acid concentration), it is necessary to choose attentively the degree of extractant loading in every particular case (pH and lactic acid concentration during fermentation).

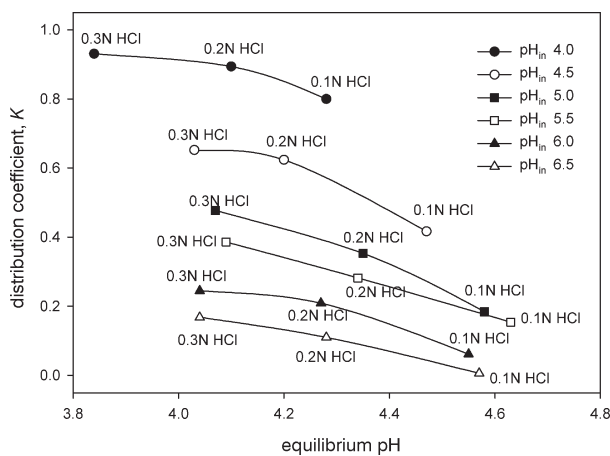


Fig. 6 – Influence of degree of TOA loading with HCl on the lactic acid extraction (organic phase:  $\varphi = 30\%$  TOA, 20% decanol, 50% dodecane) at higher initial pH. Initial lactic acid concentration  $10 \text{ g l}^{-1}$ ; initial pH 4.5–6.5.

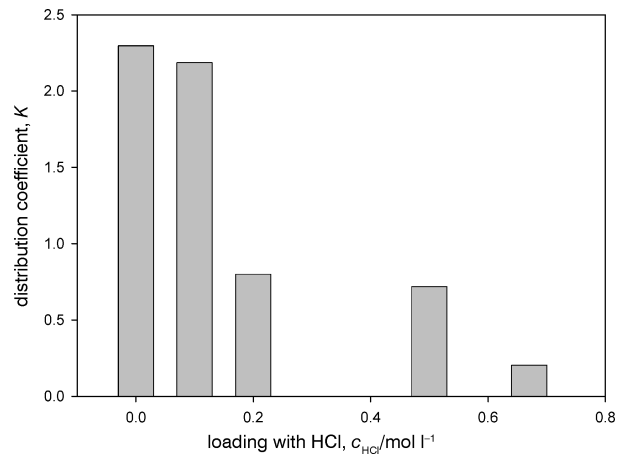


Fig. 7 – Influence of degree of TOA loading with HCl on the lactic acid extraction at natural initial pH ( $\sim 2.4$  for  $10 \text{ g l}^{-1}$  lactic acid). Organic phase composition –  $\varphi = 30\%$  TOA, 20% decanol, 50% dodecane.

At natural pH for lactic acid solutions (pH  $\sim 2.4$  for  $10 \text{ g l}^{-1}$  for example) the results are opposites – maximal value of distribution coefficient was obtained with untreated TOA, decreasing with raising extractant loading with HCl (Figure 7).

In Figure 8 are shown the results for the influence of lactic acid mass concentration on  $Z$  (the

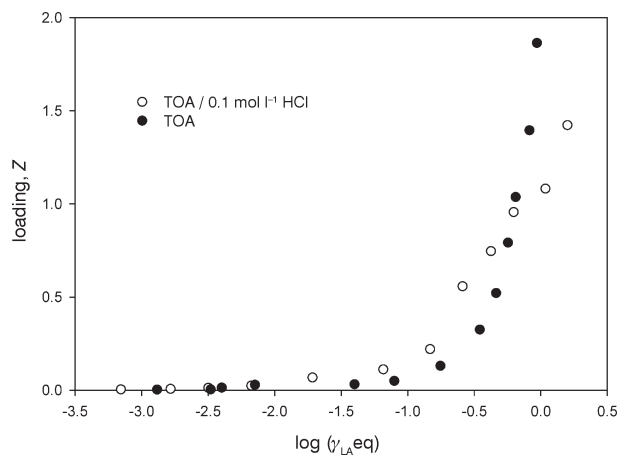


Fig. 8 – Influence of lactic acid concentration on the extraction with treated and untreated TOA (organic phase:  $\varphi = 30\%$  TOA, 20% decanol, 50% dodecane). Initial lactic acid concentrations from 0.25 to  $230 \text{ g/l}$ .

Table 1 – Initial and equilibrium pH values in case of lactic acid extraction ( $2, 3$  and  $5 \text{ g l}^{-1}$ ) with untreated and treated with  $0.05$ – $0.67 \text{ mol l}^{-1}$  HCl TOA.

Initial lactic acid concentration	Initial pH value	Equilibrium pH value				
		unloaded TOA	TOA with $0.05 \text{ mol l}^{-1}$ HCl	TOA with $0.1 \text{ mol l}^{-1}$ HCl	TOA with $0.3 \text{ mol l}^{-1}$ HCl	TOA with $0.67 \text{ mol l}^{-1}$ HCl
$2 \text{ g l}^{-1}$	5.22	5.77	5.09	4.76	4.22	3.32
$3 \text{ g l}^{-1}$	5.04	5.54	5.07	4.69	4.19	3.34
$5 \text{ g l}^{-1}$	4.72	5.18	4.71	4.53	4.09	3.26

extent to which the organic phase may be loaded with lactic acid,  $Z = \frac{[R_3NHA]}{[R_3N]_{in}}$ . Here  $[R_3NHA]$  and  $[R_3N]_{in}$  represent the acid-amine complex and initial amine mass concentrations in the organic phase. The lactic acid mass concentration varied from 0.25 to 230 g l<sup>-1</sup> and the extractant was loaded with 0.1 mol l<sup>-1</sup> HCl. One can see that up to equilibrium acid mass concentration of 2 g l<sup>-1</sup> lactic acid,  $Z$  values are equal for treated and untreated TOA, than up to 100 g l<sup>-1</sup> extraction with treated TOA is more efficient (higher  $Z$  values). It has to be mentioned that overloading (loading ratio higher than 1, i.e. complexes with more than one molecule acid for amine molecule) in case of untreated TOA is more pronounced because with treated TOA one part of extractant remains loaded with HCl, and at low pH values the ion-exchange mechanism takes a small part in the overall extraction.

#### Extraction of lactic acid from synthetic fermentation broth with TOA partially loaded with HCl

It is well known that the extraction of lactic acid with TOA at pH higher than 4.0 is very low.<sup>14,18,37,38</sup> In case of lactic acid extraction (5 g l<sup>-1</sup>) from synthetic fermentation broth (initial pH between 4.5 and 6.5) with extraction system composed from 30 % TOA, 20 % decanol and 50 % dodecane, distribution coefficient varied from 0.002 to 0.11 (Figure 9).

It has been demonstrated that for the aqueous solutions of lactic acid, partially loading of the extractant with HCl ameliorates the extraction. This approach works also in the case of simulated fermentation broth. Figure 10 presents the distribution coefficient of lactic acid as function of degree of TOA loading and initial acid concentration. It is ob-

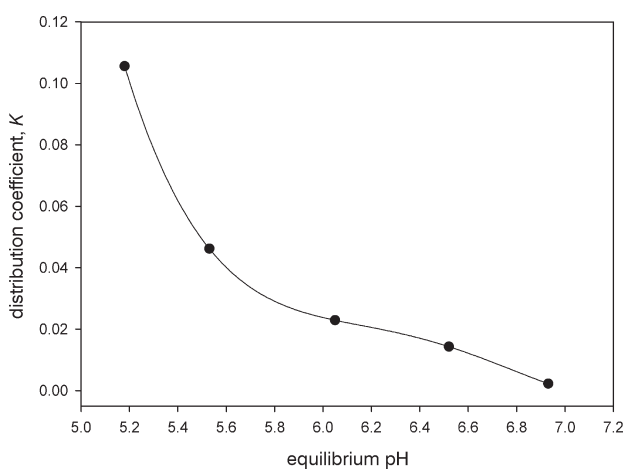


Fig. 9 – Lactic acid extraction from simulated fermentation broth with system  $\varphi = 30\%$  TOA, 20 % decanol, 50 % dodecane. Initial lactic acid mass concentration 5 g l<sup>-1</sup>; initial pH 4.5–6.5.

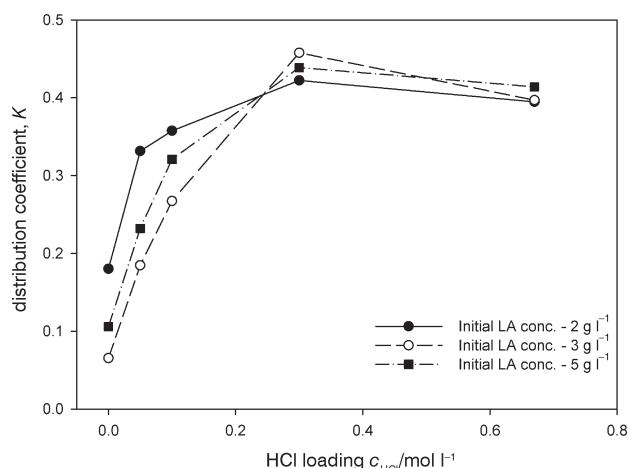


Fig. 10 – Influence of degree of TOA loading with HCl (0.05–0.67 mol l<sup>-1</sup>) and acid concentration (2–5 g l<sup>-1</sup>) on the lactic acid extraction from simulated fermentation broth. Organic phase composition –  $\varphi = 30\%$  TOA, 20 % decanol, 50 % dodecane.

vious that the treated extractant shows better performance. For all studied lactic acid concentrations maximal distribution coefficient was obtained with TOA loaded with 0.3 mol l<sup>-1</sup> HCl.

The main difference except higher distribution coefficient, between treated and untreated TOA is that in case of treated TOA the equilibrium pH is lower than initial, while with untreated, the equilibrium pH increases. (Table 1.)

When the initial pH value was adjusted to desired value (between 5.0 and 6.5, at 5 g l<sup>-1</sup> lactic acid) before extraction, the results are very similar. The best results were again obtained with TOA loaded with 0.3 mol l<sup>-1</sup> HCl (Figure 11), where the shift in equilibrium pH value was maximal. It has to be noted that the distribution coefficient has maximal values at initial pH 6.0. This result can not

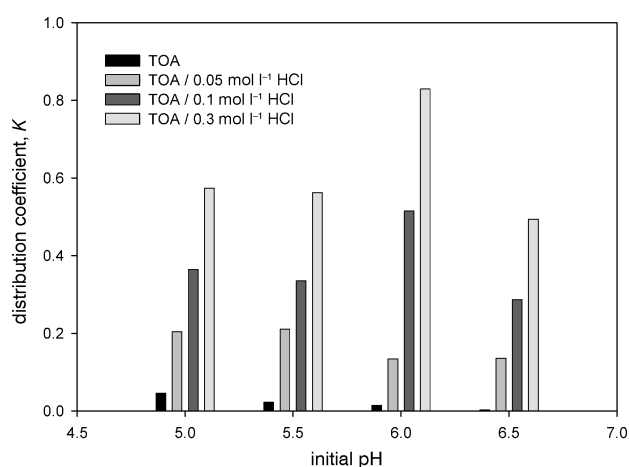


Fig. 11 – Influence of initial pH value on the extraction of lactic acid (5 g l<sup>-1</sup>) from simulated fermentation broth with treated and untreated extractant ( $\varphi = 30\%$  TOA, 20 % decanol, 50 % dodecane).

be explained with lower equilibrium pH alone. For example, distribution coefficient ( $K = 0.83$ ) for initial pH 6.0 (equilibrium pH 4.2) is greater than for the value ( $K = 0.44$ ) in case of same acid concentration without pH adjustment – initial pH 4.72 and equilibrium pH 4.09. More probably the better performance of the treated extractant in the former case is due to more pronounced share of the ion-exchange mechanism in the extraction process.

## Conclusions

The possibility of reactive extraction of lactic acid from simulated fermentation broth was examined by employing a mixed extractant, composed from Aliquat 336 and TOA.

The possibility of reactive extraction of lactic acid from aqueous solution and simulated fermentation broth was examined by employing a tertiary amine (TOA) partially loaded with HCl.

The main problem in realization of extractive fermentation – the difference between optimal pH value for fermentation and extraction and as consequence the low values of distribution coefficient can be overcome applying the mixed extractant or TOA, partially loaded with HCl.

It was demonstrated that the two proposed methods assure better performance in comparison with the free extractants.

The level of loading of TOA with HCl depends on initial concentration of lactic acid and pH value.

The best results with mixed extractant were obtained when a mixture of Aliquat and TOA at a 3:1 ratio was used.

The extraction of lactic acid with a mixed extractant leads to small changes in the pH of the solution. In all cases, the equilibrium pH value is a little bit higher than the initial one, which looks promising for realisation of *in situ* extractive fermentation.

## ACKNOWLEDGMENTS

*D. Yankov wishes to express his thanks to the Agence Universitaire de la Francophonie for the fellowship, which made the presented research possible*

## List of symbols

- $c$  – concentration, mol l<sup>-1</sup>  
 $K$  – distribution coefficient, –  
 $Z$  – loading  
 $\gamma$  – mass concentration, g l<sup>-1</sup>  
 $\varphi$  – volume fraction, %  
 $\Psi$  – volume ratio,  $\varphi_{\text{Aliquat}} / \varphi_{\text{TOA}}$

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