Recovery of aconitic and lactic acids from simulated aqueous effluents of the sugar-cane industry through liquid–liquid extraction

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Abstract: The recovery of aconitic and lactic acids from dilute aqueous effluents of the sugar-cane industry by a solvent extraction technique has been investigated in order to reduce environmental pollution and in view of the possible uses of pure solutes in the field of foods and pharmaceuticals. Reactive extraction of carboxylic acids with tributylphosphate dissolved in dodecane was examined. Experiments were performed at 25 °C for three extractant concentrations of 50%, 60% and 70% (mass%) in dodecane. The decrease of specific gravity and viscosity of solvent resulting from the presence of an inert diluent was favourable to the phase settling and the mass transfer. The percentage of acids recovered in the organic phase for a volumetric solvent ratio varying from 0.5 to 5.0 was determined. Taking into account the difference between the partition coefficients for the carboxylic acids under consideration, the selectivity of solvent with regard to aconitic acid also was quantified. Moreover, owing to its water-insolubility, its availability and its low cost, tributylphosphate can be considered as a promising extractant for large-scale applications.

Keywords: solvent extraction; aconitic and lactic acids; tributylphosphate extractant; environmental protection; water pollution

1 INTRODUCTION

Reversible chemical complexation implemented through liquid-liquid extraction method was effective for the recovery of carboxylic acids from various dilute aqueous effluents.¹⁻³ Because of the inherently acidic nature of solutes under consideration, organic Lewis bases are a potentially attractive class of extractants. The nature of complexation equilibria mean that partition coefficients are highest for low solute concentrations and the extraction capacity of the solvent is only limited by the stoichiometry of the reaction. Thus, we have explored the possibilities of tributylphosphate as extractant to remove aconitic and lactic acids from a waste product of the distillation of fermented juices and molasses of sugar-cane. With no exception, only the undissociated form of acid was extracted by this type of solvent. In the case of a phosphorus-bonded oxygen donor extractant, the phosphoryl group is a stronger Lewis base than traditional carbon-bonded oxygen donor solvents such as ketones, alcohols and ethers which give low partition coefficients with carboxylic acids.^{1,4-6} However, the relatively high viscosity of tributylphosphate $(3.56 \times 10^{-3} \text{Nsm}^{-2} \text{ at } 298 \text{K})$ and the fact that its specific gravity is close to unity (0.98) require the use of a diluent. Normally, polar diluents enhance the extracting power of the solvent but often are more soluble in the aqueous phase than non-polar compounds.⁷ In this study, pure dodecane was selected as diluent because of its low viscosity $(1.15 \times 10^{-3} \text{Ns})$ m^{-2} at 298K), its low specific gravity (0.75) and its insolubility in water. Since dodecane is chemically inert with regard to the transfer of solute in organic phase, the percentage of tributylphosphate in the system 'extractant+diluent' should be as high as possible. Taking into consideration the experimental values of viscosity and specific gravity of solvent, mentioned in Table 1, the corresponding mixtures were envisaged for the batch extraction experiments. For a concentration of tributylphosphate higher than 70 vol%, the physical properties of solvent are not compatible with a good phase settling. In this work, the distribution of aconitic acid and lactic acid

Table 1. Specific gravities and viscosities of tributylphosphate (TBP) + do-decane (D) binary mixtures at 25 $^\circ\text{C}$

TBP ratio (vol/vol)	Specific gravity	Viscosity (N s m^{-2})
50/50	0.85	2.54
60/40	0.87	2.35
70/30	0.91	1.95

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between organic and aqueous phases has been studied as regard to its dependence on the acid concentration in the aqueous solution and also the tributylphosphate content in the solvent. The influence of solvent ratio upon the efficiency of the extraction process was mainly examined because this factor has economic significance in establishing the conditions of design.⁸ Over the past few years, only the citric acid extraction process has been carried through to major production.^{9a,9b}

2 MATERIALS

Tributylphosphate, dodecane, aconitic and lactic acids were provided by Aldrich Chemical Co and were analysed by HPLC in order to verify their purity, which was close to 99%. However, lactic acid, a concentrated aqueous solution which contains 15 mass % of water, must be distilled using a total reflux condenser for 12h in order to hydrolyse dimers present in the solution.^{10,11} Deionised water produced by a Millipore Mille-Q Water System was used in this work. The pK_a values of aconitic and lactic acids^{12,13} are listed in Table 2.

3 EXPERIMENTAL PROCEDURE

Based on the average concentration of acids in waste water of sugar cane industry,¹⁴ two initial aqueous solutions of various acid concentrations were treated by solvent extraction. The first solution contained 1.7 mass % of aconitic acid and 0.4 mass % of lactic acid (pH=1.5) while the second was composed of 0.3 mass% of aconitic acid and 0.4 mass% of lactic (pH=1.7). With regard to the solvent composition, the tributylphosphate concentration should be as high as possible since the diluent does not affect the extraction capacity of the solvent. Taking the phase separation into consideration three types of mixtures 'extractant+diluent' containing 50 mass %, 60 mass % and 70 mass % of tributylphosphate respectively were studied. The solvent was saturated with water because small amounts of water enhance solvation for the acid solute. This phenomenon appears to be associated with formation of complexes in which water molecules serve as hydrogen-bonded bridges between the carboxylic acid and the protonaccepting solvent.⁷ With regard to the liquid-liquid systems under consideration, the specific gravity and the viscosity of solvent were compatible with good

Table 2. pK_a values of aconitic and lactic acids

Carboxylic acid	pK_a (in aqueous solution at 25°C)	
Aconitic	$pK_{a_1} = 2.80$ $pK_{a_2} = 4.46$ $pK_{a_3} = 6.30$	
Lactic	p <i>K</i> _a =3.86	

settling of the phases. For batch extraction experiments, both aqueous and organic phases were mixed in glass-stoppered separation funnels maintained at a steady temperature of $25(\pm 1)$ °C for 3h. This time represents a sufficient shaking period to obtain the maximum percentage of solute extracted by the solvent. After a settling time of 1.5h, the phases were separated and analysed by High Performance Liquid Chromatography (HPLC) which gives the concentration of solutes in each of them. With regard to the organic phase, a stripping of carboxylic acids with H_2SO_4 solution (0.5 M) was necessary before introducing samples into the analysis apparatus. The HPLC method consisted of a pump (Spectra-Physics SP 8800), an integrator (Chromjet SP 4400), a UV spectrophotometer (Spectra 100 UV-V is detector: wavelength=210nm) and an organic acid column (Bio-Rad Aminex ion exclusion HPX-87H) operated at 41 °C. The mobile phase was $0.005 \text{ M} \text{ H}_2 \text{SO}_4$ and its flow rate was $0.6 \text{ cm}^3 \text{ min}^{-1}$. The analyses were made immediately after the batch extraction assays in order to avoid possible oxidation by air, evaporation or a bacteriological degradation of the samples. Three replications of extraction experiments were necessary to confirm the validity of results obtained in this work. The accuracy relative to the percentages of extracted acids and the purities of aconitic acid in the extract (Figs 1-6) was estimated to be 2% for all batch experiments.

4 RESULTS AND DISCUSSION

Some authors^{1,15,16} have shown that undissociated molecules of carboxylic acids were only extracted by the organophosphorus solvent. Consequently, the distribution of organic acids between the solvent and the aqueous phase essentially depends on the strength of the acids.

Since the pH values of the initial aqueous solutions are lower than the pK_a of aconitic and lactic acids (Table 2), these solutes were mainly in molecular form in aqueous phases. In the case of aconitic acid, the first dissociation constant essentially determines the strength of the acid, the contribution of others being rather marginal. Thus, aconitic acid which is relatively stronger than lactic acid will be more dissociated whatever the pH values of both initial aqueous solutions. On the other hand, since the hydrophilicity of the acid radical is increased by hydroxyl functional groups, the differences in partition coefficient values for various solutes are often significant.¹ Thus the hydroxyl functional group present in lactic acid strongly depresses its extractibility by the organic solvent. Indeed, from dilute aqueous solutions containing less than 2.0 mass % for an individual acid and a solvent composed of the mixture 'tributylphosphate (70 vol%) + dodecane (30 vol%)', the partition coefficients, determined from liquid-liquid equilibrium, at the temperature of 25°C, were 12.7 for aconitic acid and 2.9 for lactic acid. Furthermore, the difference between the free energies of phase transfer of two acids obtained from experimental results is about $6 \text{ kJ} \text{ mol}^{-1}$. The more basic donor properties of the phosphorus-bonded oxygen than those of the carbon-bonded oxygen render the solvation process specific. The number of extractant molecules (*n*) per carboxylic group of organic acid in the extract is experimentally accessible. The distribution of the undissociated carboxylic acid (HA) between the organic phase (o) and the aqueous phase (w) involves the dissociation of the acid in aqueous solution HA \leftrightarrow H⁺+A⁻ and the formation of acid solvates in organic phase with *n* moles of tributylphosphate (TBP) following the equation:

$$HA_{(w)} + nTBP_{(o)} - HA^{T}TBP_{n(o)}$$

The solvation constant (Ke) was defined as the ratio:

$$Ke = [HA^{T}BP_n]_{(0)}/[HA_{(w)}][TBP]^n_{(0)}$$

In the case of a weak carboxylic acid, at a pH value of aqueous solution lower than the pK_a of the individual acid, the plot of the logarithm of partition coefficient (*m*) against the logarithm of the tributylphosphate concentration in the organic phase ([TBP]_(o)), yields a straight line, the slope corresponds to the solvation number (*n*) and the intercept to the solvation constant (*Ke*):

$$\log(m) = \log(Ke) + n \log([\text{TBP}]_{(0)})$$

In this expression, the partition coefficient for an individual acid (m) is defined by the ratio of molar concentrations of the acid in the organic and the aqueous phases at equilibrium. [TBP](0) represents the molar concentrations of free tributylphosphate in the extract. With regard to the carboxylic acids under consideration, an experimental study of liquid-liquid equilibrium¹⁷ permitted the calculation of the solvation numbers for aconitic and lactic acids, which were found to be 2.3 and 1.3 respectively. However, previous works showed that a stoichiometric association between the individual phosphoryl group of tributylphosphate and the individual carboxyl group of various acids exists in the organic phase.^{1,15} Furthermore, in the presence of a solvating reagent such as tributylphosphate, there are no unsolvated acid species in the organic phase and no acid dimers can be formed in the extract since this organophosphorus compound is a much stronger acceptor than the carbonyl oxygen of the acid's carboxyl group. The influence of the volumetric solvent ratio as well as the effect of the concentration of tributylphosphate in the mixture 'extractant+diluent' both on the percentage of extracted acid and the selectivity of the extraction process were examined. With regard to the batch extraction experiments (Figs 1-6), the percentages of acid solutes (mass%) extracted by the solvent were calculated in relation to the amount of these acids present in the initial aqueous solutions. The purity of



Figure 1. Recovery of aconitic and lactic acids by saturated solvent 'tributylphosphate (50 vol%) + dodecane (50 vol%)' at 25 °C. Influence of solvent ratio (initial aqueous phase: aconitic acid (1.7 mass%) + lactic acid (0.4 mass%)).

aconitic acid was defined as the ratio of the amount of aconitic acid in the organic phase compared with the total quantity of two acids in the same phase, called 'extract'. From an initial aqueous solution containing 1.7 mass % of aconitic and 0.4 mass % of lactic acid, the percentage of aconitic acid extracted with a volumetric solvent ratio of 5 was more than 99% but the purity in the extract does not exceed 85% (Figs 1-3). On the other hand, the purity of aconitic acid in the organic phase was about 90% for a low solvent ratio of 1 but the amount of the acid extracted was less than 85%. Thus, whatever the tributylphosphate concentration in the solvent there is always a compromise between the quantity of solute transferred in the organic phase and its purity in the extract. From an initial aqueous solution containing 0.3 mass% of aconitic acid and 0.4 mass % of lactic acid, the purity of aconitic acid in the extract was about 50% whatever the volumetric solvent ratio and the tributylphosphate content in the system 'tributylphosphate+dodecane'. With a volumetric solvent ratio of 5, the percentage of aconitic acid extracted changes from 97.4 mass % to 99.7 mass % when the percentage of extractant varies from 50 mass% to 70 mass% (Figs 4-6). Further-



Figure 2. Recovery of aconitic and lactic acids by saturated solvent 'tributylphosphate (60 vol%) + dodecane (40 vol%)' at 25 °C. Influence of solvent ratio (initial aqueous phase: aconitic acid (1.7 mass%) + lactic acid (0.4 mass%)).



Figure 3. Recovery of aconitic and lactic acids by saturated solvent 'tributylphosphate (70 vol%)+dodecane (30 vol%)' at 25 °C. Influence of solvent ratio (initial aqueous phase: aconitic acid (1.7 mass%))+ lactic acid (0.4 mass%)).



Figure 4. Recovery of aconitic and lactic acids by saturated solvent 'tributylphosphate (50 vol%)+dodecane (50 vol%)' at 25 °C. Influence of solvent ratio (initial aqueous phase: aconitic acid (0.3 mass%))+ lactic acid (0.4 mass%)).



Figure 5. Recovery of aconitic and lactic acids by saturated solvent 'tributylphosphate (60 vol%)+dodecane (40 vol%)' at 25 °C. Influence of solvent ratio (initial aqueous phase: aconitic acid (0.3 mass%)+ lactic acid (0.4 mass%)).

more, the liquid–liquid extraction process would be useful only if the solvent can be easily recycled. Indeed the extractant recovery cycle significantly affects the design of the whole process. In the present study, a back-extraction of aconitic and lactic acids was performed at 25 °C. The solutes were stripped from



Figure 6. Recovery of aconitic and lactic acids by saturated solvent 'tributylphosphate (70 vol%)+dodecane (30 vol%)' at 25 °C. Influence of solvent ratio (initial aqueous phase: aconitic acid (0.3 mass%))+lactic acid (0.4 mass%)).

the solvent through three successive contacts with a sodium hydroxide solution (0.1 M). From a volumetric ratio of alkaline solution to the organic phase of 2, the recovery of both acids in aqueous solution was close to 100%. An economical regeneration of solvent was considered as an important factor with regard to the large-scale development of the extraction process.

5 CONCLUSIONS

A solvent extraction technique based on the dissociation-extraction concept has been proposed as an alternative to the conventional precipitation process to remove and separate carboxylic acids from dilute aqueous effluents. The experimental results obtained in this work (Figs 1-6) bear out that tributylphosphate appears to be an efficient extractant with regard to the recovery of carboxylic acids. However, the viscosity and the specific gravity of pure tributylphosphate need to be reduced in order to avoid excessive energy consumption and to improve the phase settling in continuous extractors. Furthermore, the implementation of an extraction process using a solvent, like for example tributylphosphate which is very slightly miscible in aqueous phase (0.039 mass%), allows us to minimise pollution of the environment.

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