Universidade de Aveiro Departamento de Química

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FILIPE SERRÃO SANTOS OLIVEIRA

EXTRACÇÃO DE MATERIAIS DE PLATAFORMA DE BIORREFINARIA COM LÍQUIDOS IÓNICOS

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Dissertação apresentada à Universidade de Aveiro para cumprimento dos requisitos necessários à obtenção do grau de Mestre em Materiais Derivados de Recursos Renováveis, realizada sob a orientação da Doutora Isabel Maria Delgado Jana Marrucho Ferreira, Professora Auxiliar do Departamento de Química da Universidade de Aveiro

Este trabalho é dedicado às três pessoas mais importantes da minha vida, os meus pais e a minha irmã, aos quais devo tudo.

o júri

presidente

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Agradecimentos

Os meus agradecimentos mais sinceros à Prof. Isabel Marrucho por acreditar em mim, pela forma como me motiva e que me desafia a fazer melhor todos os dias, pelo conhecimento transmitido e pela contribuição para o meu crescimento pessoal e profissional. Ao Prof. Luís Paulo Rebelo pela oportunidade de desenvolver o meu trabalho no Laboratório de Termodinâmica Molecular no ITQB II. Ao Dr. José Esperança e aos restantes membros do Laboratório de Termodinâmica Molecular do ITQB II, em especial ao João Araújo, ao Rui Ferreira, à Ana B. Pereiro e à Helga Garcia pela ajuda e convívio prestados ao longo do trabalho.

Aos membros do Path da Universidade de Aveiro em especial à Mara Freire, à Catarina Neves e à Ana Rute Ferreira pela ajuda prestada com o COSMO-RS.

À minha família, os meus incríveis pais e irmã, à minha grande avó, primos, tias e tio espectaculares e ao meu fantástico grupo de amigos.

Palavras-chave

Ácido láctico, ácido málico, ácido succínico, extracção, líquidos iónicos, coeficientes de partição, COSMO-RS.

Resumo

O crescimento económico sustentável requer a garantia de recursos para a produção industrial. O desenvolvimento de biorrefinarias representa a chave para o acesso a uma produção integrada de alimentos, rações, produtos químicos, materiais, mercadorias e combustíveis do futuro.

O objectivo deste trabalho é avaliar a capacidade de extracção de materiais de plataforma de biorrefinaria utilizando líquidos iónicos. Para tal efeito, foram seleccionados ácidos orgânicos de cadeia curta, tais como os ácidos L-láctico, L-málico e succínico, que são produzidos por via fermentativa em soluções aquosas diluídas, e utilizados líquidos iónicos à base do catião fosfónio com cadeias alquílicas relativamente longas. Foi avaliado o efeito de três parâmetros nos coeficientes de partição e na eficiência de extracção: a natureza do anião do líquido iónico, a temperatura do processo e a concentração do ácido na solução aquosa de partida. Foram ainda testadas duas metodologias de recuperação dos ácidos em estudos: alteração de pH e destilação a pressão reduzida. O método computacional de previsão COSMO-RS foi também utilizado para prever o equilíbrio de fases dos sistemas ternários, água+ácido orgânico+líquido iónico, em estudo tendo-se obtido resultados satisfatórios.

Keywords Lactic acid, malic acid, succinic acid, extraction, ionic liquids, partition coefficient, COSMO-RS.

Abstract

Sustainable economical growth requires safe resources of raw materials for the industrial production. Petroleum is today's most frequently used industrial raw material, which is neither sustainable, nor environmentally friendly.

While the economy of energy can be based on various alternative raw materials, such as wind, sun, water, biomass, the economy of substances is fundamentally depending on biomass, in particularly on biomass of plants. The development of biorefineries represents the key for the access to an integrated production of food, feed, chemicals, materials, goods and fuels of the future.

Special requirements are placed to both, the substantial converting industry as well as research and development regarding the efficiency of the bio-based product line as well as sustainability. The objective of this work is to evaluate the extraction capacity of phosphonium-based ionic liquids regarding biorefinery platform materials, focusing on small chain organic acids such as L-lactic, L-malic and succinic acids. The effect of three parameters on the partition coefficients and on the efficiency of extraction was evaluated: the ionic liquid anion's nature, the temperature of the process and the concentration of the acid in the start aqueous solution. Two different approaches to recover the organic acid from the ionic liquid were rehearsed with good results. The predictive capacity of the COSMO-RS for the ternary systems water+organic acid+ionic liquid was evaluated.

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List of Abbreviations and Symbols

ACN	Acetonitrile
atm	Atmosphere
$Conc_{AQ}$	Concentration of acid in the aqueous phase
$Conc_{i0}$	Initial concentration of acid
$Conc_{IL}$	Concentration of acid in the ionic liquid phase
$Conc_{NQ}$	Concentration of acid non-quantified
EE %	Extraction Efficiency in percentage
HPLC	High Performance Liquid Chromatography
ILs	Ionic Liquids
Kp	Partition Coefficient
LCF	Lignocellulose Feedstock
$[P_{6\,6\,6\,14}][Cl]$	Tetradecyltrihexylphosphonium chloride
$[P_{6\,6\,6\,14}][Dec]$	Tetradecyltrihexylphosphonium decanoate
$[P_{6\,6\,6\,14}][Phos]$	Tetradecyltrihexylphosphonium bis(2,4,4-trimethylpentyl)phosphinate
PBS	Poly(butylene succinate)
PET	Poly(ethylene terephthalate)
PMLA	Poly(malic acid)
PLA	Poly(lactic acid)
PS	Poly(styrene)
PVC	Poly(vinyl chloride)
T	Temperature
TBP	Tri-*n*-butylphosphate
TCA	Tricarboxylic acid
TOA	Tri-*n*-octylamine
TOPO	Tri-*n*-octylphosphineoxide
UV / Vis	Ultraviolet / Visible
VOCs	Volatile Organic Compounds
wt %	Weight percentage

1. INTRODUCTION

1.1 General Context

The discovery of crude oil, in the 19th century, changed the world's source of energy and fuels from renewable to the fossil and non-renewable resources. This fact led to a faster industrialization and improved the standards of living, but the rapid consumption of the resources posed new problems. According to Kenneth S. Deffeyes[1], the world has already reached its maximum production of crude oil, also known as "Hubbert's Peak", in 2005 and soon the crude oil reserves will be scarce. Nowadays, a large number of alternative energy replacement options already exist, with special emphasis on those based on natural renewable resources like wind, sunlight, water and biomass. However, until now none of these resources has a feasible exploitation process that can ashore the world's demand of energy and fuel.[2] Biomass presents the potential to meet the challenges of sustainable and green energy systems, mostly due to its complex composition, similar to petroleum. Its main constituents are carbohydrates, lignin, proteins and fats, along many other substances, such as vitamins, dyes, flavors and aromatic essences, which confers biomass very different chemical structures. In addition, biomass already exists as product, the key difference between petroleum, which is obtained by extraction. [3]

In order to produce useful chemicals and fuels from biomass, a system similar to a petroleum refinery, called "biorefinery", has been proposed. The biorefinery systems can be distinguished by their feedstock. For example, the 'Whole Crop Biorefinery' uses raw material such as cereals, the 'Green Biorefinery', uses 'nature-wet' biomasses such as green grass, lucerne, clover, or immature cereal, and the 'Lignocellulose Feedstock (LCF) Biorefinery' uses 'nature-dry' raw material, such as cellulose-containing biomass and wastes. The LCF biorefinery is the system that might become the most successful, since it can have feedstock at competitive prices and presents a relative homogeneity of composition, being capable of processing a wide variety of feedstock in the same plant. [4]

Biorefineries allow the production of bio-fuels as well as building-block chemicals from biomass. Organic acids constitute a key group among the building-block chemicals that can be produced by fermentation processes with biomass as feedstock. Most of them are natural products of microorganisms, or at least natural intermediates in major metabolic pathways. Organic acids are extremely useful as starting materials for the chemical industry. For many organic acids the actual market is small, but new sustainable production processes will create new markets and provide new opportunities for the

chemical industry. For example, succinic, fumaric and malic acid are potential replacements for the petroleum-derived commodity chemical maleic anhydride. The market for maleic anhydride is huge with a volume of 213 000 tons per year, whereas the current production for the organic acids mentioned is small ranging from 10 to 16 000 tons per year. This fact is due to price limitations, since these acids are still produced industrially through a chemical route from non-renewable feedstock. However, once a competitive fermentation production process for one of these acids is established the market for that acid will increase. On the other hand, some organic acids, like lactic acid, already have a feasible fermentation production process, where biomass can be used as feedstock: lactic acid has an annual production of 150 000 tons all via fermentation route. Other acids like acetic, itaconic, gluconic and citric are also produced by fermentation processes at an industrial scale.[5] Nevertheless, the design of efficient separation processes of these acids from dilute waste water and fermentation broths is rather difficult because of the strong affinity of the organic acid to water, increasing the overall cost of the their production via fermentation by at least 50%. The high solubility in water renders traditional organic solvents to be successfully used for the extraction of the produced acids. Unfortunately, the use of organic solvents brings up some associated problems such as toxicity, volatility and flammability, and implies additional environmental hazards.[6]

The most commonly used organic solvents to extract organic acids from dilute aqueous solutions are tri-*n*-butylphosphate (TBP), tri-*n*-octylamine (TOA) and tri-*n*-octylphosphineoxide (TOPO), which can be used pure or as a mixture with other organic solvents such as hexanol, octanol, decanol, ethyl acetate, kerosene and dodecane, among others. However, poor results were obtained, with partition coefficients close to the unit.[7-8] At a moment, when pollution is a topic of general concern, increased awareness and strict regulations, the development of new green solvents has been receiving increased attention from academia and industrial areas. Among these alternative solvents ionic liquids (ILs) play a central role as potential substitutes of volatile organic compounds. Ionic liquids have already been tested in the separation of L-lactic acid from aqueous solutions. Typically hydrophobic ILs were used as pure solvents, diluted in organic solvents or with the addition of extractants such as TOA. So far, the most promising approach regarding the use of pure ILs as L-lactic acid extractants is the use of phosphonium-based ILs with long alkyl side chains due to their very low solubility in aqueous solutions.

The main objective of this work is to test the efficiency of the ionic liquids to extract three short chain organic acids (L-lactic, L-malic and succinic) from dilute aqueous solutions, as a raw model of using ionic liquids to extract bioproducts from fermentation broths where they are produced. In the following sub-chapters the three organic acids which are the subject of this study are briefly introduced as well as their synthetic routes and their applications. An overview of ionic liquids properties which distinguish this class of compounds from the commonly used volatile organic solvents is then presented. In the end, the thermodynamic definition of partition coefficient and the experimental methodologies used to determine it are discussed.

1.2 Organic Acids as Platform Materials

1.2.1 Lactic Acid

Lactic acid is considered to be an important compound that participates in several biochemical processes. For example, in the human body lactate is constantly produced and eliminated during normal metabolism and physical exercise.[9] Lactic acid is the simplest hydroxyl acid and presents an asymmetric carbon atom, which generate two optically active configurations, the L and D isomers (Figure 1). It can be found in many fermented food products both naturally or as a product of *in situ* microbial fermentation, as in sauerkraut, yogurt, buttermilk, sourdough breads among others.[10]

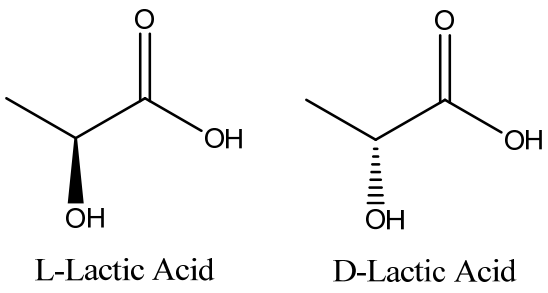


Figure 1. Isomers L-Lactic acid and D-Lactic acid.

In the end of the 19th century, lactic acid started to be produced on an industrial scale essentially by two producers using distinct processes, CCA Biochem that used carbohydrate feedstocks and fermentation technology, and Sterling Chemicals that used a chemical synthesis to produce lactic acid.[10]

The fermentative process uses renewable feedstocks, such as glucose and maltose from corn or potato, or sucrose from cane or beet sugar among others, as raw materials. The fermentation of the sugars is carried out with bacteria at a very slow rate, taking normally 4 to 6 days to be complete. Then carbon is added to the resulting fermentative broth to remove colored impurities, and also calcium carbonate ($CaCO_3$) to promote the formation of calcium lactate. The salt solution is filtered, generating a large amount of solid waste. The recovered calcium lactate present in the resulting solution is still much diluted (approximately 10% concentrated), therefore requiring an evaporation step to concentrate the salt (which involves a lot of energy). By acidification and further distillation, lactic acid is produced. However, the lactic acid produced by this process has only technical grade purity, which is only suitable for some applications. In order to achieve a product with a similar purity to the one accomplish by chemical synthesis, an extra esterification purification process is required, which leads to higher energy consumption.[11] The separation and purification processes are the barriers to cost-effective production of lactic acid from fermentation processes.[10]

There are two fermentation processes that can be used depending on the type of bacteria used, the hetero-fermentative and the homo-fermentative. Nevertheless, only the second one is used in industrial processes, since it leads to greater yields of lactic acid (> 90 %) and lower concentration of secondary products. The *Lactobacillus* is the most common species of bacteria used in the homo-fermentation processes. Depending on the organism used for the fermentation, the L isomer, the D isomer or a mixture of both can be obtained. Organisms such as *Lactobacilli amylophilus* , *L. bavaricus* , *L. casei* and *L. maltaromicus*, produce mostly the L isomer, whereas, *L. delbrueckii* , *L. jensenii* or *L. acidophilus* produce the D isomer or the racemic mixture.[12]

The chemical synthesis of lactic acid uses non-renewable starting materials and it begins with the reaction of hydrogen cyanide (HCN) with acetaldehyde

(CH_3CHO). The product of this reaction is 2-hydroxypropanenitrile, also known as lactonitrile, and it is then isolated by distillation and hydrolyzed by sulfuric acid (H_2SO_4). This step produces an ammonium sulfate by-product that reduces the atom economy of the reaction to 60%. The resulting lactic acid undergoes then an esterification with methanol followed by distillation, hydrolysis and further distillation in order to isolate an extremely high purity lactic acid. Both lactic acid production processes pose real issues concerning the relative greenness of the process. The fermentation route uses renewable resource feedstock presenting lower hazard potential, but it generates high amount of waste (although benign) and requires high energy consumption. The chemical route is based on a non-renewable resource as feedstock and presents higher potential hazard than the fermentation route since the waste produced is non-benign. Nevertheless, the majority of the world-wide production of lactic acid implemented nowadays comes from renewable resources.[11]

The growth in the production of lactic acid extended its applications from the medical area to food industry, cosmetics, pharmaceuticals and the polymer industry. Lactic acid is used in the food industry to produce emulsifying agents and is used in foods, particularly for bakery goods and also as an acidity regulator, flavoring, pH buffering agent or inhibitor of bacterial spoilage in a wide variety of products such as candy, breads and bakery products, soft drinks, soups, sherbets, dairy products, beer, jams and jellies, mayonnaise, processed eggs among others. In pharmaceutical and cosmetic industries, lactic acid is use in lotions and biodegradable polymers. Before the lactic acid biodegradable polymers were used only for medical applications such as surgical sutures, controlled-release drugs and prostheses, now there are also used for food packaging and in the textile industry.

Today, lactic acid is considered to be one of the primary platform materials (Figure 2).[10, 12]

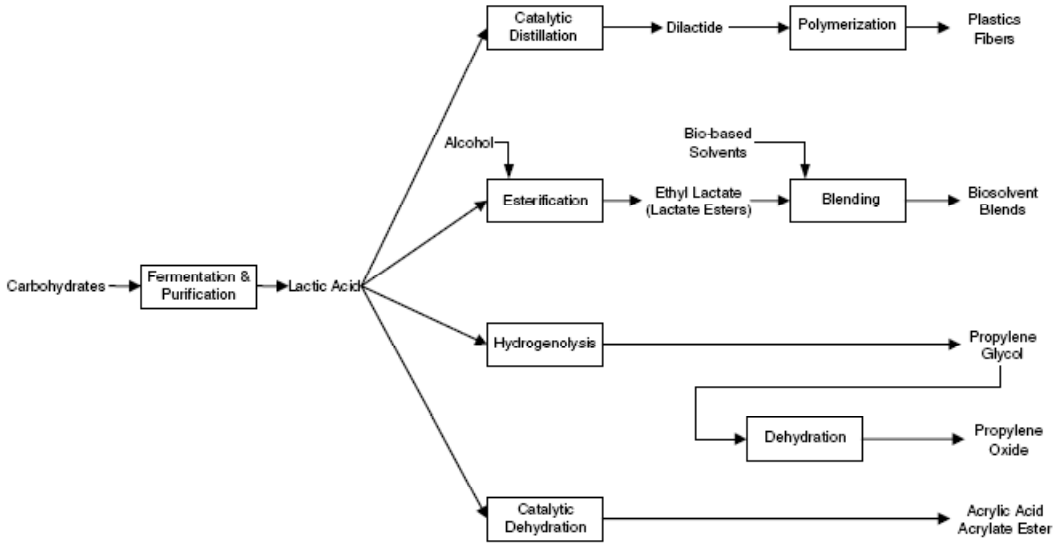


Figure 2. Lactic acid-based potential products and uses.[10]

However, its most attractive use is the production of poly(lactic acid) (PLA). Literature related to PLA has increased exponentially over the past decade, which can be partly attributed to the "green" movement that is stimulating the use of bio-based polymers, being PLA one of the most promising at the moment. It can be processed with many techniques and has a large-scale production. It is relatively cheap and has some remarkable properties, like its good processability, biocompatibility and biodegradability. Furthermore, due to the presence of the isomers L and D in the production of lactic acid, it can lead to the manufacture of polymers with different physical properties, depending on the ratio of L/D-Lactic acid used, making PLA suitable for different applications.[9-10, 12]

Although PLA has been produced since around 1970 as a high-value material, its use was limited to biomedical applications (implants, sutures, drug encapsulation, among others) because of its high production cost. Nowadays, PLA is used in a wider range of products mainly in the packaging and textile industry, due to the breakthrough in the polymerization of high molecular height PLA, which was only achieved in the early 1990s by Cargill Inc.[11] Currently, PLA polymers and co-polymers are viewed as the potential substitutes for some petrochemical-based polymers, such as polystyrene (PS), poly(ethylene terephthalate) (PET) or

poly(vinyl chloride) (PVC), since they present good mechanical properties along with many possible applications.[10]

1.2.2 Succinic Acid

Succinic acid (Figure 3) is a common metabolite of plants, animals and microorganisms. It is an important C_4 dicarboxylic acid building block, widely recognized as a potential platform chemical for the production of various value-added derivatives.[13-14]

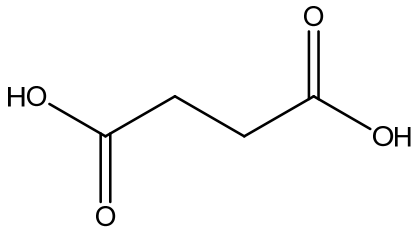


Figure 3. Succinic acid chemical structure.

Nowadays, succinic acid is commonly used as a surfactant, detergent or foaming agent, and also in the food industry (as an acidity regulator, flavoring agent or anti-microbial agent) as well as in health-related products for pharmaceuticals and antibiotics formulation.[5] It is mainly produced by chemical route from *n*-butane via the maleic anhydride, using the C_4-fraction of naphtha. The maleic anhydride is hydrogenated to succinic anhydride, which is then hydrated to produce succinic acid. [15-16]

Succinic acid can be also produced via fermentation route using expensive commercial glucose as raw material, which increases the production costs when compared with the traditional chemical production processes. Nevertheless, the importance of succinic acid as a major platform material has encouraged scientists to found ways to reduce the fermentation costs. The use of renewable raw materials as feedstock in the bioproduction of succinic acid is one possible solution. This

important step allowed the production of less expensive succinic acid that can be used as a platform material in the production of biodegradable polymers.[13, 16]

Succinic acid is an intermediate of the tricarboxylic acid cycle (TCA) and one of the fermentation end-products of anaerobic metabolism. Over the years, many different types of microorganisms have been tested for the production of succinic acid, like fungi (different *Aspergillus stc.*, *Byssochlamys nivea*, *Lentinus degener*, *Paecilomyces varioti*, *Penicillium viniferum*), yeast (*Saccharomyces cerevisiae*) and Gram-positive bacteria (*Corynebacterium glutamicum*, *Enterococcus faecalis*). *Anaerobiospirillum succiniciproducens* and *Actinobacillus succinogenes* are the most studied bacteria in the production of succinic acid since they can use a wide variety of carbon sources such as glucose, glycerol, sucrose, maltose, lactose, and fructose.[17-18] However, the main problems associated with the use of these bacteria are the high concentrations of by-products like acetic, propionic and pyruvic acids, leading to increased costs in the product purification.[16]

Liu et al.[19] using *Actinobacillus succinogenes* achieved a productivity of 1.15 $g \cdot L^{-1} \cdot h^{-1}$ of succinic acid form cane molasse, producing 55.2 $g \cdot L^{-1}$ of succinic acid. Lee et al. [20] used a new bacteria, *Mannheimia succiniciproducens* MBEL55E, that was isolated as a natural succinic acid overproducer from bovine and claimed to have a productivity of 3.9 $g \cdot L^{-1} \cdot h^{-1}$ of succinic acid. Additionally, studies with recombinant Escherichia coli strains, which can enhance succinic acid production under both aerobic and anaerobic conditions, have been developed.[15, 21-23] Lin et al.[22] used E. coli under strict aerobic conditions to efficiently produce and accumulate succinate, producing 58.3 $g \cdot L^{-1}$ with an average productivity of 1.08 $g \cdot L^{-1} \cdot h^{-1}$. More recently, Meynial-Salles et al.[24] introduced a new step to remove the end products from the fermentation broth, which enhanced growth, productivity and final product concentration. The maximum productivity reached was of 10.4 $g \cdot L^{-1} \cdot h^{-1}$ and a final concentration of 83 $g \cdot L^{-1}$ of succinic acid.

As a building block, succinic acid can replace the petroleum-derived maleic anhydride and also be used as a precursor for the production of other compounds like diamines or diols, which are used to produce a wide range of polymers, like polyamides (ex. Nylon), polyesters (ex. poly(butylene succinate) – PBS) and poly(ester amide)s (Figure 4). [5, 16]

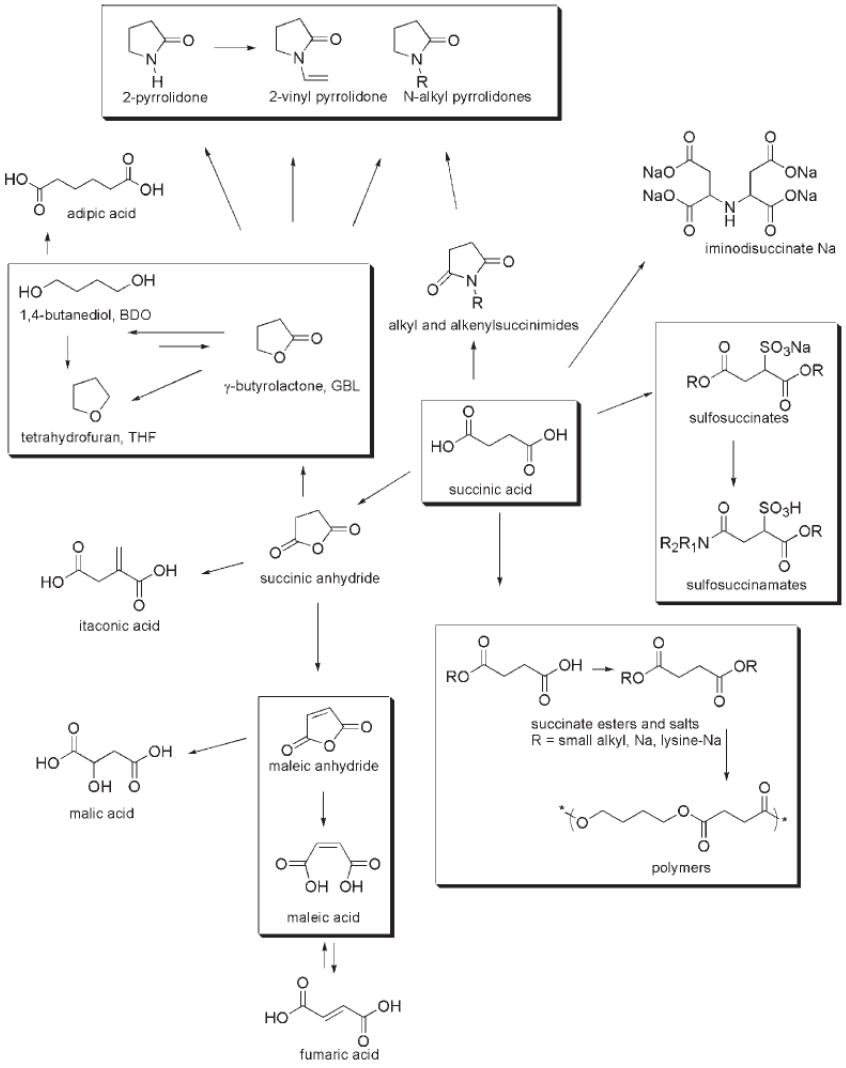


Figure 4. Succinic acid derived products by chemical conversion.[25]

1.2.3 Malic Acid

Malic acid is a C_4 hydroxy dicarboxylic acid, presenting 2 isomers the L-Malic acid and the D-Malic acid (Figure 5). It is also an intermediate metabolite in the TCA cycle of living cells.[26]

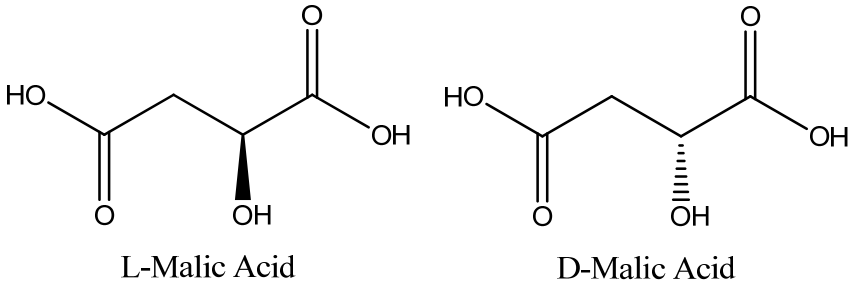


Figure 5. Isomers L-Malic acid and D-Malic acid.

This acid is known for its great tartness and taste retention, which makes it a commonly used food additive. It also has other important applications in other fields like the polymer, cosmetic and pharmaceutical industries. Moreover, L-malic acid is efficiently used in the treatment of liver dysfunction and hyperammonemia.[27]

Currently, malic acid is synthesized via a petrochemical route from maleic anhydride, but it can also be synthesized by a fermentation process, since it was identified as a product of yeast fermentation in 1924. Nowadays, the organisms found that can produce higher malic acid concentrations are *Saccharomyces cerevisiae* and *Zygosaccharomyces rouxii*, which can produce up to 59 and 75 $g \cdot L^{-1}$ respectively.[28]

In 2004, the U.S. Department of Energy included malic acid in the top 12 most interesting chemical building blocks that can be derived from biomass, along with other 1,4-dicarboxylic acids, such as succinic and fumaric acids. These three organic acids are viewed as potential replacements for the maleic anhydride, which is a petroleum-derived commodity chemical.

Malic acid is also the monomeric precursor of poly(malic acid) (PMLA). PMLA is a completely biodegradable polymer with attractive properties, such as its biocompatibility, bioresorbability and non-toxicity, for application in the nanobiotechnology and biomedicine fields. It is soluble in water and certain organic solvents due to the reactivity of its pendant carboxylic groups. Since PMLA production costs are still fairly high, its properties and applications have not been extensively investigated yet. Nevertheless, it seems to have a promising future as

drug carrier due to its easy metabolism in a living body. The presence of a pendant carboxylic group that can easily bind to other functional groups, enables an easy introduction of various drugs into its polymeric chain.[29-30]

1.3 Ionic Liquids

In recent years ionic liquids (ILs) have grown to be one of the most studied classes of solvents and are considered as valid potential substitutes of many volatile organic solvents. ILs are salts, thus ionic compounds, that are liquid bellow a conventional temperature of 373 K.[31] This is due to the asymmetry and charge dispersion of their organic and inorganic ions. Among other unique thermophysical properties ILs do not evaporate at ambient conditions,[32] present relatively high thermal stability, high ionic conductivity and large liquidus temperature range. Moreover, ILs exhibit excellent solvent qualities for many types of compounds (polar and non-polar), a fact that stems from the notion that their physical/chemical properties can be finely adjusted by a careful selection of ions, which, in turn determines an interplay between Coulombic, van der Waals, and specific, mainly space-oriented, interactions.[33] This fact enables the optimization of yield, selectivity, substrate solubility, product separation and even enantioselectivity.[31-35]

All of these properties potentiate the ILs use in a wide range of areas, such as physical chemistry, electrochemistry, engineering, material sciences, analytics, solvents and catalysts and even biological uses.[36] Among all of these foreseeable applications for ILs, there has been considerable interest in their use in separation processes, namely in the liquid-liquid extraction of organic compounds from water. Since ILs present negligible vapor pressure, it allows the extracted product to be separated from the ionic liquid by low-pressure distillation (potential for energy savings) with the recovery of the IL for reuse. Therefore, the replacement of conventional organic solvents by ionic liquids in extraction processes is seen as a promising field of investigation.[37]

The extraction of aromatic compounds from water with different imidazolium-based ILs was studied by Huddleston et al. [38] and Freire et al.[39] In another work, McFarlane et al. [40] using imidazolium and phosphonium-based ionic liquids presented partition coefficients for a number of organic solutes and discussed the possibilities and limitations of common volatile organic compounds for extraction from aqueous media.

Recently, the extraction of fermentation products with ionic liquids has been suggested.[6] Among all the considered products, lactic acid has received special attention mainly due to its large application in a wide variety of fields. Matsumoto et al.[6] studied the extraction of lactic acid, along with other organic acids, with imidazolium-based ionic liquids, but the results were not satisfactory due to the low partition coefficients obtained (below 1), whereas Marták et al. [41-43] shown that phosphonium-based ionic liquids could prove to be effective extractants of lactic acid, achieving partition coefficients above 40 at low lactic acid concentrations. The extraction of organic products and/or metabolites from aqueous media requires ILs with low solubility in water since the higher the IL hydrophobicity is, the higher their extractive potential will be.[44] The phosphonium-based ILs are known for they high hydrophobic character and the ability to form micelles, especially when large alkyl chain lengths are present. Marták et al.[42] were able to identify the presence of reversed micelles in IL trihexyltetradecylphosphonium bis(2,4,4-trimethylpenthyl)phosphinate water saturated solutions.

1.4 Partition Coefficients

When a substance is added to a system of two immiscible liquids, it will distribute itself between the two solvents until the equilibrium is reached, meaning that the ratio of the concentrations of the substance in the two phases becomes constant. As illustrated in Figure 6, for a given solute X distributed between two immiscible solvents I and II, the partition or distribution ratio, also called distribution constant or coefficient is defined by equation 1.[45]

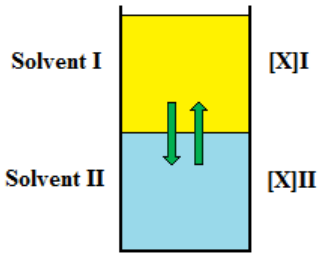


Figure 6. Distribution of solute X in a mixture of two immiscible solvents.

$$K_{p1} = \frac{[X]_I}{[X]_{II}} \quad (1)$$

This "partition law" is not verified in several systems. For instance, it does not apply to the distribution of benzoic acid in the mixture of benzene-water, due to the formation of benzoic acid dimmers in the benzene phase, leading to the presence of more than one chemical species in solution. The same reasoning can be used in the determination of the distribution of substances that ionize in aqueous solution. Hence, the partition coefficient needs to be defined for each work in a convenient and clear way so that the final objectives can be accomplished. For example, it can be defined regarding the same molecular species or the summation of all the molecular species derived from a first one in both phases.

There are two different partition coefficients measuring methods: the direct methods, which directly quantify the solute in one or both phases of the system, and the indirect methods, where a direct quantitative analysis is nor performed but instead a calibration curve is usually used.[45] In this work a direct method, the shake flask method, was applied since it is the most used. This method consists on dissolving the solute in one of the phases and then the second phase is added and the mixture vigorously stirred in order to distribute the solute between both phases. After the stirring, the two phases are separated and the amount of solute in each one of them quantified. The most used analytical methods of quantification are the spectrophotometry (UV/Vis) and high performance liquid chromatography (HPLC). The accuracy of the obtained results can be directly linked to the high purity of the solvents and solute, the low concentrations of solute and also to the pre-saturation of the solvents, one in the other. [45]

1.5 Scope and Objectives

In this work, the capacity of hydrophobic ILs to extract small chain organic acids was evaluated. L-lactic, L-malic and succinic acid, all considered to be platform chemicals that can be derived from renewable resources using the appropriate biotechnological processes, were the subject of the present study. This research work aims at developing a more benign process of extraction of these small chain organic acids, than those used nowadays. Nowadays, these acids are usually produced via a fermentation route, but the extraction procedure presently used relies on conventional volatile organic compounds (VOC's), which leads up to several problems such as toxicity, volatility and flammability, and implies additional environmental hazards. Recently, ILs have been receiving increased attention as a potential and alternative replacement for VOC's, due to their negligible vapor pressures and their good solvation and thus extraction properties. Moreover, their negligible vapor pressures (undoubtedly the most attractive physical property), reduces environmental pollution and working exposure hazards.

Phosphonium-based ILs were selected to be used as extractants in the present study due to their hydrophobic character which makes them virtually insoluble in water, as thus easy to separate. These ILs already have shown better results in the extraction of organic acids than the imidazolium-based.[40-41, 46-47] The effect of using three different anions, chloride, decanoate and bis(2,4,4-trimethylpenthyl)phosphinate, as well as several experimental parameters that could affect the extraction efficiency such as temperature of extraction and the concentration of the acid used in the starting solution, were also evaluated.

2. EXPERIMENTAL SECTION

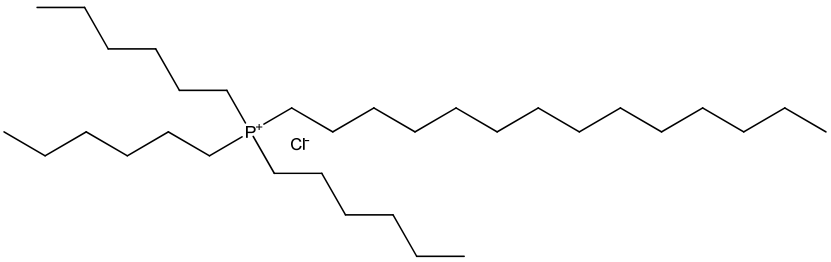
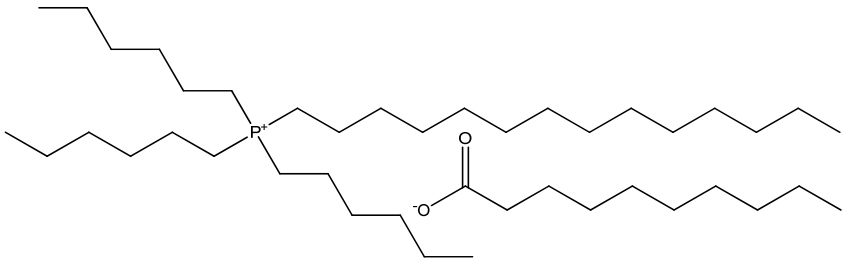
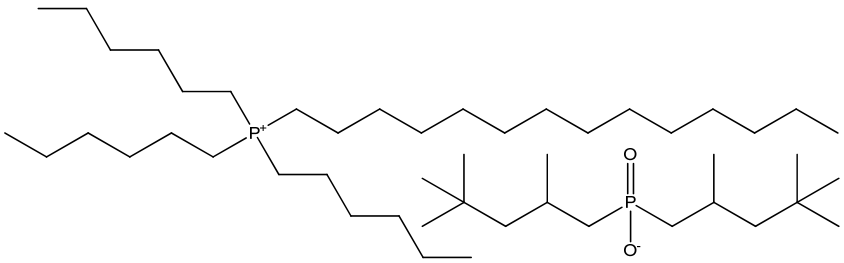
2.1 Materials

The L-lactic acid was acquired in an aqueous solution with mass fraction purity between 79-81% at Fluka. L-malic acid was also acquired at Fluka, in the solid state with mass fraction purity higher than 99.5%. Succinic acid, also in the solid state, was purchased at Sigma-Aldrich with mass fraction purity higher than 99.0%.

The water used for the preparation of acid solutions was double-distilled, passed through a reverse osmosis system and finally treated with a Milli-Q plus 185 water purification apparatus.

The chemical structures of the ILs used and corresponding designations are presented in Table 1. Tetradecyltrihexylphosphonium chloride ([P_{66614}][Cl], CAS 258864-54-9), tetradecyltrihexylphosphonium decanoate ([P_{66614}][Dec], CAS 465527-65-5) and tetradecyltrihexylphosphonium bis(2,4,4-trimethylpentyl)phosphinate ([P_{66614}][Phos], CAS 465527-59-7) were kindly provided by CYTEC Industries. All the ILs were dried under constant stirring at moderate temperatures (maximum of 333 K) and under vacuum for a minimum of 24 h. Since all of these ILs are extremely hygroscopic[44], this step is crucial in order to reduce volatile impurities, as well as water, which can be considered as an impurity and affect the ILs properties.[48-49] The water content in the ILs was determined by Karl-Fisher titration (Metrohm 831 Karl Fischer coulometer) after the drying procedure and was found to be smaller than 5×10^{-4} in mass fraction. The purity of the three ILs were further checked by ^{1}H, ^{13}C and ^{19}F NMR spectra as reported in Appendix A. Tetradecyltrihexylphosphonium chloride, tetradecyltrihexylphosphonium decanoate and tetradecyltrihexylphosphonium bis(2,4,4-trimethylpentyl)phosphinate presented mass fraction purities of 99 %, 97 % and 94 % respectively. No further purification of the ILs was carried out.

Table 1. List of ionic liquids used, their chemical structure and respective abbreviation.

IL Designation	Chemical Structure
Tetradecyltrihexyl phosphonium chloride $[P_{6\,6\,6\,14}][Cl]$	
Tetradecyltrihexyl phosphonium decanoate $[P_{6\,6\,6\,14}][Dec]$	
Tetradecyltrihexyl phosphonium bis(2,4,4-trimethylpentyl) phosphinate $[P_{6\,6\,6\,14}][Phos]$	

2.2 Apparatus and Procedure

Aqueous solutions of L-lactic, L-malic and succinic acids were prepared with concentrations in range of 0.05-0.5 M. The pH of the each acid aqueous solution was evaluated, using pH-indicator strips. All solution presented pH values lower than 3, above the acids' first pK_a (Table 2). Thus, all the acids are in their undissociated form.

Table 2. Dissociation constants for lactic, malic and succinic acids at 298 K.[50]

Compound	pK_{a1}	pK_{a2}
Lactic Acid	3.86	–
Malic Acid	3.40	5.11
Succinic Acid	4.21	5.64

For the preparation of the lactic acid solution, a previous distillation with total reflux of the distillate for at least 12 hours was required, in order to split the acid dimmer. Afterwards, the solution was kept in the cold (277.15 K) in order to prevent the dimmer formation.[51]

For the extraction procedure, conic falcon tubes with a magnetic spinner inside were used. Using a pipette, the IL (*circa* 0.8 g) was added to the acid solutions inside the tube, in a proportion of 1:1 (v/v) forming a two phase system. The mixture was then stirred until an emulsion was formed using a Labnet Vortex mixer, and then kept under vigorous stirring for at least 10 h in a IKA RET Basic plate. This time period was previously tested and found to be enough to achieve equilibrium. In order to control the temperature of extraction, an ethyleneglycol-water mixture was used as refrigerant fluid in the extractions at 308 K and 313 K. For the extractions at 288 K a refrigerated water bath was used. To break the emulsions, the falcon tubes were centrifuged for 1 hour at 3750 rpm at the same temperature of the extraction.

After the separation of the ionic liquid and aqueous phases which compose the emulsion, a sample of both phases was taken with a syringe. The amount of acid present in both phases was quantified using a HITACHI Elite LaChrom HPLC, with a Diode Array Detector L-2455, using an UV light at a wavelength of 210 nm, which is the wavelength of maximum absorbance of these organic acids. [52-53] The chromatographic quantification of the acid in both phases was done using an optimized procedure, by a injecting 50 μL of sample in a Phenomenex Luna 5u C18 (2) 100A column (250 × 3 mm), with 5 μm particle size. The elution was isocratic with a mixture of 60 % acetonitrile – 40 % buffer solution (0.00625 M aqueous solution of H_2SO_4) in volume, the column temperature was kept as 313 K and the flow was constant at 0.1 $mL \cdot min^{-1}$.

An optimization of the eluent was also required. At first, an aqueous solution of H_2SO_4 (0.0025 M) was use as eluent. The aqueous phase samples were diluted in water and the ionic liquid phase samples were first diluted in acetone and then in water. However, due to the similarity of the acetone and acids retention time, this method did not work. Samples were analyzed with different flow rates in the range between 0.05 and 1 $mL \cdot min^{-1}$ but no significant changes were obtained. The second trial was performed using an acetonitrile (ACN) solution of H_2SO_4 (0.0025 M) and both samples were diluted in pure acetonitrile. In order to reduce the amount of acetonitrile used, solubility tests of the three ILs in acetonitrile-water mixtures with different compositions were conducted. It was found that the mixture composition of 60 % ACN – 40 % water in volume was able to dissolve all ILs. The pH of this mixture was measured and was found to be approximately 2 at 298 K, which is above all the acids' first pKa. In this way, the quantification of all acids both ionic liquid and aqueous samples was done using the mixture 60 % ACN – 40 % buffer solution (0.00625 M aqueous solution of H_2SO_4) in volume as eluent.

A calibration curve was established for each acid under study. This calibration curve was used to calculate the concentration of the acids in both aqueous and ionic liquid phases. Table 3 presents the calibration parameters for all acids. Further details are reported in Appendix B.

Table 3. Calibration curve's parameters for the studied organic acids.

Compound	Slope ($\times 10^{-10}$)	Correlation Coefficient (R^2)
L-Lactic Acid	8.5454	0.9988
L-Malic Acid	9.6551	0.9982
Succinic Acid	6.7083	0.9980

In order to determine each acid partition coefficients between the aqueous and the ionic liquid phase and the respective standard deviations, a minimum of three replicas of the same sample were quantified. The acids retention times are presented in Table 4. Although the ILs presented purities in agreement with standard procedures, some impurities were present in the elution zone of the acids. An extraction just using IL + water

was carried out as a blank. The same procedure was used at four different temperatures: 288 K, 298 K, 308 K and 313 K.

Table 4. Retention times of the studied organic acids.

Compound	Retention Time / min
L-Latic Acid	11.3
L-Malic Acid	10.7
Succinic Acid	11.2

3. RESULTS AND DISCUTION

The quantification of the three acids was accomplished in both the aqueous ($Conc_{AQ}$) and the ionic liquid ($Conc_{IL}$) phases, as reported in Tables 5, 6 and 7 for the L-lactic, L-malic and succinic acids, respectively. In some cases the amount of acid quantified in both phases is smaller than the initial amount used in the extraction, $Conc_{i0}$, and thus a column with the non-quantified fraction, $Conc_{NQ}$, was added in Tables 5, 6 and 7. In some cases, the emulsion could not be completely broken even after the centrifugation and the presence of a spongy interface between the IL phase and the aqueous phase was visually detected, as it can be observed in Figure 7. This fact was also registered in the last column of Tables 5, 6 and 7 in order to help in the interpretation of the results. A multi-step extraction procedure, which will be detailed later, confirmed that this spongy interface contained acid that can be further extracted.

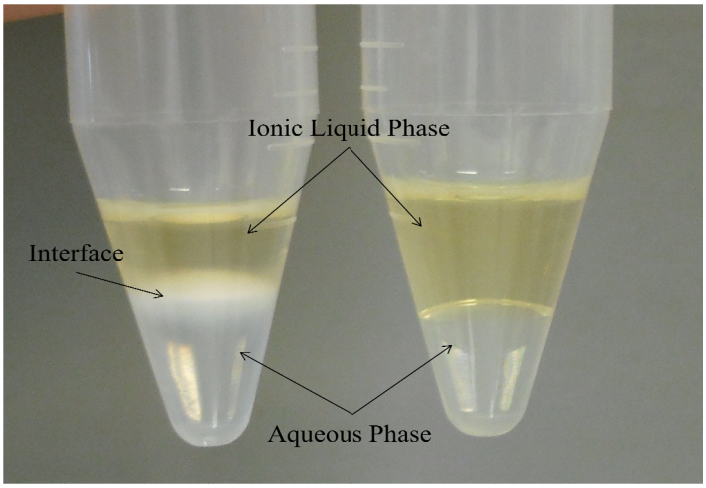


Figure 7. Presence and absence of interface in the extraction of L-lactic acid with concentrations of 0.50 M (left) and 0.05 M (right) when $[P_{66614}][Phos]$ was used.

From the analysis of Tables 5, 6 and 7 it can be concluded that in general the presence of the interface depended on two factors: the IL used and the organic acid extracted. Among the acids, L-lactic acid promoted the presence of an interface in aqueous solutions of two ILs, $[P_{6\,6\,6\,14}][Dec]$ and in $[P_{6\,6\,6\,14}][Phos]$, while succinic acid was the only acid that promoted interface in aqueous solutions of $[P_{6\,6\,6\,14}][Cl]$. L-malic acid seems to be the acid that had the least ability to preserve the micelles in the studied ionic liquids.

It was also observed that in general this interface was thicker when lactic acid solutions are used than for solutions of the other two acids. Thus, it is evident that the presence of the different acids affected in different ways the stability of the phosphonium-based IL reversed micelles. The presence of reversed micelles in ILs has already been reported in literature.[41-42, 54-55] Marták et al.[41-42] reported the formation of reversed micelles in phosphonium-based ILs as a water extraction mechanism into the solvent, suggesting that the lactic acid was extracted by the formation of complexes with the IL and water. These authors do not describe the formation of an interface between the two phases of the system.

Although the temperature and the acid concentrations investigated did not significantly influence the presence of the interface, they affected its thickness. In general, the interface's volume increased with increasing acid concentration and decreasing temperature. This increased stability with the increasing concentration of a 3rd species and decreasing temperature is also observed in the large majority of the surfactants.[56]

Nevertheless, it can also be observed in Tables 5, 6 and 7 that even when no interface was observed the mass balance of the acid in the two phases could not be closed. The largest deviations were found for L-malic acid and $[P_{6\ 6\ 6\ 14}][Phos]$, where losses around 40 % were obtained for the initial concentrations of 6.73, 13.45 and 26.90 g of acid/g of solution at 298.15 K. The other acids presented smaller deviations. L-lactic acid presented a loss of 23 % for the $[P_{6\ 6\ 6\ 14}][Dec]$ at 288.15 K with a initial concentration of 45.20 g of acid/g of solution. For the $[P_{6\ 6\ 6\ 14}][Cl]$, the mass losses of L-lactic acid varied from 2 to 11 % and in the $[P_{6\ 6\ 6\ 14}][Phos]$ case the losses varied between 11 and 19 %. Succinic acid also presented the highest loss with $[P_{6\ 6\ 6\ 14}][Dec]$, 34 % at 313.15 K and 5.93 g of acid/g of solution. For the $[P_{6\ 6\ 6\ 14}][Dec]$ IL, succinic acid presented losses between 23 and 25 % at 298 K while for the $[P_{6\ 6\ 6\ 14}][Phos]$ the losses varied from 14 to 28 %. Some authors defended the formation of complexes between the lactic acid and the surfactant (IL in this work) used for its extraction. For example, Martak et al.[42] proposed the formation of complexes, aggregates, between the IL, lactic acid and water, with the following stechiometry $(LAH)_x(IL)(H_2O)_2$ where x = 1, 2 or 3. Thus, the extraction of lactic acid would take place through a dual mechanism: the formation of reverse micelles with encapsulation of the acid and the formation of complexes that are preferably extracted to the organic phase.

Table 5. Quantification of the extracted L-lactic acid. Concentration is expressed in g of solute/ g of solution.

IL	T (K)	$Conc_{i0}$ (g/g) × 10^3	$Conc_{IL}$ (g/g) × 10^3	$Conc_{AQ}$ (g/g) × 10^3	$Conc_{NQ}$ (g/g) × 10^3	Interface Presence
$[P_{6\,6\,6\,14}]$ [Cl]	288.15	45.20	27.32 ± 0.12	13.17 ± 0.16	4.71	No
	298.15	4.52	2.63 ± 0.00	1.73 ± 0.00	0.17	No
		9.04	5.46 ± 0.06	3.07 ± 0.03	0.51	No
		18.08	11.11 ± 0.33	5.57 ± 0.08	1.41	No
		45.20	28.10 ± 0.03	16.35 ± 0.10	0.75	No
	308.15	45.20	27.45 ± 0.30	14.03 ± 0.10	3.73	No
	313.15	45.20	25.02 ± 0.36	15.12 ± 0.29	5.06	No
$[P_{6\,6\,6\,14}]$ [Dec]	288.15	45.20	32.20 ± 0.18	2.35 ± 0.03	10.56	No
	298.15	4.52	2.67 ± 0.05	0.03 ± 0.00	1.82	Yes
		9.04	5.45 ± 0.17	0.02 ± 0.00	3.57	Yes
		18.08	11.17 ± 0.22	0.14 ± 0.00	6.78	Yes
		45.20	29.89 ± 0.26	1.21 ± 0.00	14.10	Yes
	308.15	45.20	34.21 ± 0.30	1.78 ± 0.03	9.21	Yes
	313.15	45.20	30.61 ± 0.14	1.24 ± 0.02	13.36	Yes
$[P_{6\,6\,6\,14}]$ [Phos]	288.15	45.20	33.31 ± 0.78	2.24 ± 0.01	9.65	Yes
	298.15	4.52	3.05 ± 0.08	0.98 ± 0.01	0.49	No
		9.04	6.32 ± 0.01	0.96 ± 0.02	1.76	No
		18.08	14.47 ± 0.02	1.24 ± 0.00	2.38	No
		45.20	37.85 ± 0.30	2.09 ± 0.01	5.26	Yes
	308.15	45.20	35.31 ± 0.11	2.09 ± 0.03	7.80	Yes
	313.15	45.20	36.85 ± 0.23	1.90 ± 0.00	6.45	No

Table 6. Quantification of the extracted L-malic acid. Concentration is expressed in g of solute/ g of solution.

IL	T (K)	$Conc_{i0}$ (g/g) × 10^3	$Conc_{IL}$ (g/g) × 10^3	$Conc_{AQ}$ (g/g) × 10^3	$Conc_{NQ}$ (g/g) × 10^3	Interface Presence
$[P_{6\,6\,6\,14}]$ [Cl]	288.15	6.73	5.03 ± 0.05	0.49 ± 0.01	1.20	No
	298.15	6.73	5.64 ± 0.10	1.06 ± 0.03	0.02	No
		13.45	10.17 ± 0.15	3.27 ± 0.07	0.02	No
		26.90	20.28 ± 0.25	6.39 ± 0.12	0.23	No
		67.26	41.31 ± 1.18	20.27 ± 0.44	5.67	No
	308.15	6.73	5.59 ± 0.05	1.07 ± 0.01	0.07	No
	313.15	6.73	4.89 ± 0.13	0.62 ± 0.05	1.22	No
$[P_{6\,6\,6\,14}]$ [Dec]	288.15	6.73	4.79 ± 0.14	0.26 ± 0.01	1.68	No
	298.15	6.73	5.38 ± 0.16	0.02 ± 0.00	1.33	No
		13.45	8.86 ± 0.19	0.01 ± 0.00	4.58	Yes
		26.90	14.17 ± 0.08	0.02 ± 0.00	12.71	Yes
		67.26	47.18 ± 0.70	0.11 ± 0.01	19.97	Yes
	308.15	6.73	4.87 ± 0.16	0.89 ± 0.02	0.97	No
	313.15	6.73	4.13 ± 0.15	0.64 ± 0.01	1.95	No
$[P_{6\,6\,6\,14}]$ [Phos]	288.15	67.26	55.64 ± 0.02	1.49 ± 0.05	10.12	No
	298.15	6.73	4.03 ± 0.10	0.07 ± 0.00	2.63	No
		13.45	7.91 ± 0.01	0.31 ± 0.00	5.24	No
		26.90	16.45 ± 0.02	0.37 ± 0.00	10.09	No
		67.26	54.89 ± 0.19	0.26 ± 0.00	12.10	Yes
	308.15	67.26	58.71 ± 0.39	1.58 ± 0.02	6.97	No
	313.15	67.26	58.91 ± 0.19	1.42 ± 0.03	6.93	No

Table 7. Quantification of the extracted succinic acid. Concentration is expressed in g of solute/ g of solution.

IL	T (K)	$Conc_{i0}$ (g/g) × 10^3	$Conc_{IL}$ (g/g) × 10^3	$Conc_{AQ}$ (g/g) × 10^3	$Conc_{NQ}$ (g/g) × 10^3	Interface Presence
$[P_{6\,6\,6\,14}]$ [Cl]	288.15	5.93	4.37 ± 0.04	0.46 ± 0.07	1.09	Yes
	298.15	5.93	5.30 ± 0.10	0.50 ± 0.01	0.12	Yes
		11.85	10.26 ± 0.12	1.19 ± 0.01	0.40	Yes
		23.71	20.37 ± 0.18	2.04 ± 0.04	1.30	Yes
		59.27	48.15 ± 0.10	7.59 ± 0.04	3.53	No
	308.15	5.93	5.28 ± 0.09	0.57 ± 0.01	0.08	Yes
	313.15	5.93	4.65 ± 0.14	0.51 ± 0.02	0.76	Yes
$[P_{6\,6\,6\,14}]$ [Dec]	288.15	5.93	3.85 ± 0.10	0.62 ± 0.01	1.46	No
	298.15	5.93	4.79 ± 0.08	0.13 ± 0.00	1.01	Yes
		11.85	8.79 ± 0.04	0.28 ± 0.00	2.78	No
		23.71	17.38 ± 0.15	0.40 ± 0.04	5.92	No
		59.27	45.75 ± 0.39	0.14 ± 0.01	13.38	No
	308.15	5.93	4.60 ± 0.04	0.87 ± 0.00	0.45	No
	313.15	5.93	3.76 ± 0.04	0.13 ± 0.00	2.03	No
$[P_{6\,6\,6\,14}]$ [Phos]	288.15	5.93	3.84 ± 0.01	0.50 ± 0.02	1.59	No
	298.15	5.93	5.31 ± 0.11	0.18 ± 0.01	0.43	Yes
		11.85	9.59 ± 0.07	0.60 ± 0.01	1.66	No
		23.71	18.48 ± 0.05	0.74 ± 0.02	4.47	No
		59.27	49.40 ± 0.44	1.18 ± 0.01	8.69	No
	308.15	5.93	3.82 ± 0.06	0.43 ± 0.00	1.67	No
	313.15	5.93	4.09 ± 0.02	0.34 ± 0.00	1.50	No

The analysis of the obtained results leads to the conclusion that the acid can be extracted to the IL rich phase in two forms: the free form (when the micelle's mechanism is present) and in the complex form (when complexes are formed). Nevertheless, only the acid in the free form was quantified. On top of this, the acid that was not extracted to the ionic liquid phase can be in the aqueous phase or/and in the spongy phase (interface). Since, in the present case, only the free acid (and not the acid in the complexes) was monitored, the partition coefficients are determined according to:

$$K_{p2} = \frac{[Acid]_{IL}}{[Acid]_{AQ} + [Acid]_{NQ}} \quad (2)$$

where $[Acid]_{IL}$ is the concentration of organic acid quantified in the ionic liquid phase, $[Acid]_{AQ}$ is the concentration of organic acid quantified in the aqueous phase and $[Acid]_{NQ}$ is the concentration of organic acid that was not quantified. In most of the literature[57-59] the amount of solute is only quantified in the aqueous phase and it is assumed that the rest was extracted to the ionic liquid phase. In this case the partition coefficients are determined according to equation 3.

$$K_{p3} = \frac{[X]_{i0} - [X]_{AQ}}{[X]_{AQ}} \quad (3)$$

The partition coefficients calculated by equations 1, 2 and 3 for the three acids are presented in Tables 8, 9 and 10. Another parameter calculated was the efficiency of the extraction which is given by equation 4.

$$EE\ (\%) = \frac{[Acid]_{IL}}{[Acid]_{i0}} \quad (4)$$

Table 8. Partition coefficients for the L-lactic acid.

IL	T (K)	$Conc_{i0}$ (M)	Kp_1	Kp_2	Kp_3
$[P_{6\,6\,6\,14}]$ [Cl]	288.15	0.50	2.07	1.53	2.43
	298.15	0.05	1.52	1.39	1.62
		0.10	1.77	1.52	1.94
		0.20	2.00	1.59	2.25
		0.50	1.72	1.64	1.76
	308.15	0.50	1.96	1.55	2.22
	313.15	0.50	1.65	1.24	1.99
$[P_{6\,6\,6\,14}]$ [Dec]	288.15	0.50	13.73	2.50	18.21
	298.15	0.05	85.23	1.44	143.52
		0.10	227.55	1.52	376.56
		0.20	82.57	1.61	132.70
		0.50	24.62	1.95	36.24
	308.15	0.50	19.27	3.11	24.46
	313.15	0.50	24.68	2.10	35.46
$[P_{6\,6\,6\,14}]$ [Phos]	288.15	0.50	14.87	2.80	19.17
	298.15	0.05	3.10	2.07	3.60
		0.10	6.58	2.32	8.41
		0.20	11.71	4.00	13.64
		0.50	18.12	5.15	20.64
	308.15	0.50	16.90	3.57	20.64
	313.15	0.50	19.41	4.41	22.81

Table 9. Partition coefficients for the L-malic acid.

IL	T (K)	$Conc_{i0}$ (M)	Kp_1	Kp_2	Kp_3
$[P_{6\,6\,6\,14}]$ [Cl]	288.15	0.05	10.23	2.97	12.67
	298.15	0.05	5.31	5.21	5.33
		0.10	3.11	3.09	3.12
		0.20	3.18	3.06	3.21
		0.50	2.04	1.59	2.32
	308.15	0.05	5.24	4.93	5.30
	313.15	0.05	7.92	2.66	9.90
$[P_{6\,6\,6\,14}]$ [Dec]	288.15	0.05	18.14	2.47	24.49
	298.15	0.05	354.18	4.01	441.41
		0.10	1463.82	1.93	2220.54
		0.20	712.17	1.11	1351.00
		0.50	441.70	2.35	628.63
	308.15	0.05	5.49	2.62	6.58
	313.15	0.05	6.45	1.59	9.50
$[P_{6\,6\,6\,14}]$ [Phos]	288.15	0.50	37.30	4.79	44.08
	298.15	0.05	56.68	1.49	93.61
		0.10	25.79	1.43	42.88
		0.20	44.83	1.57	72.33
		0.50	209.03	4.44	255.12
	308.15	0.50	37.17	6.87	41.58
	313.15	0.50	41.42	7.06	46.29

Table 10. Partition coefficients for the succinic acid.

IL	T (K)	$Conc_{i0}$ (M)	Kp_1	Kp_2	Kp_3
$[P_{6\,6\,6\,14}]$ [Cl]	288.15	0.05	9.42	2.81	11.77
	298.15	0.05	10.59	8.52	10.83
		0.10	8.59	6.44	8.93
		0.20	10.00	6.10	10.64
		0.50	6.34	4.33	6.81
	308.15	0.05	9.33	8.15	9.47
	313.15	0.05	9.05	3.65	10.53
$[P_{6\,6\,6\,14}]$ [Dec]	288.15	0.05	6.19	1.85	8.53
	298.15	0.05	36.06	4.19	43.65
		0.10	31.11	2.87	40.95
		0.20	43.86	2.75	58.79
		0.50	316.97	3.38	409.67
	308.15	0.05	5.30	3.48	5.82
	313.15	0.05	28.20	1.74	43.42
$[P_{6\,6\,6\,14}]$ [Phos]	288.15	0.05	7.63	1.84	10.78
	298.15	0.05	28.96	8.62	31.32
		0.10	15.96	4.24	18.73
		0.20	25.09	3.55	31.16
		0.50	41.79	5.01	49.14
	308.15	0.05	8.87	1.82	12.76
	313.15	0.05	12.11	2.23	16.55

From the inspection of Tables 8, 9 and 10 it can be seen that the partition coefficients values had, as expected, very large differences when calculated using the three different equations. When $[P_{6\,6\,6\,14}][Cl]$ was used all partition coefficients presented similar values for all organic acids. This is due to the low acid losses. For L-lactic and L-malic acid, this IL did not present interface and thus the losses were generally low. For the succinic acid, although the presence of an interface was noticed the amount of acid retained in it is minimum, as it can be seen in Table 7. The extraction with the other two ILs, $[P_{6\,6\,6\,14}][Dec]$ and $[P_{6\,6\,6\,14}][Phos]$, displayed in general higher losses than for $[P_{6\,6\,6\,14}]$ [Cl]. The losses in the acids quantification led to enormous differences in the values of the

partition coefficients calculated using the three different equations. Due to this fact the partition coefficients used for the discussion of this work were the ones calculated using equation 2, since it is the one that takes into account the amount of acid not quantified and also the one that presents more realistic values.

3.1 Effect of IL anion on the Partition Coefficients

The choice of the IL anions proved to have a great effect on the partition coefficients and the extraction efficiencies of the acids. Figures 8, 9 and 10 report the data obtained for the ILs $[P_{6\,6\,6\,14}][Cl]$, $[P_{6\,6\,6\,14}][Dec]$ and $[P_{6\,6\,6\,14}][Phos]$ respectively.

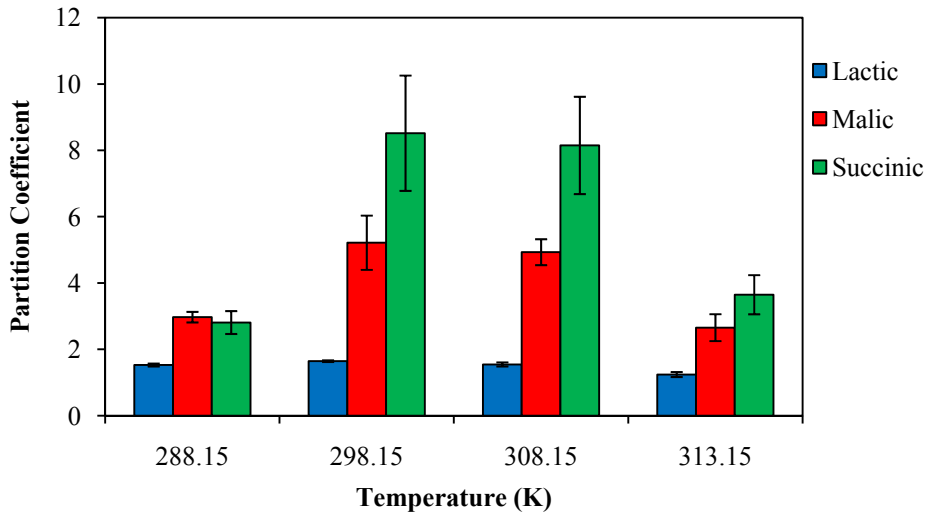


Figure 8. Effect of the anion chloride on the partition coefficients of the studied acids with temperature, at a concentration of 0.50 M for L-lactic acid and 0.05 M for L-malic and succinic acids.

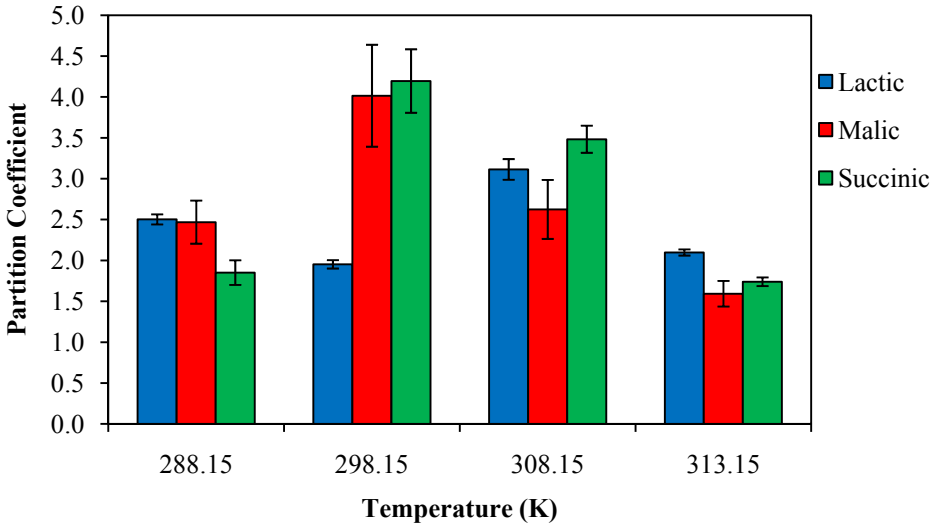


Figure 9. Effect of the anion decanoate on the partition coefficients of the studied acids with temperature, at a concentration of 0.50 M for L-lactic acid and 0.05 M for L-malic and succinic acids.

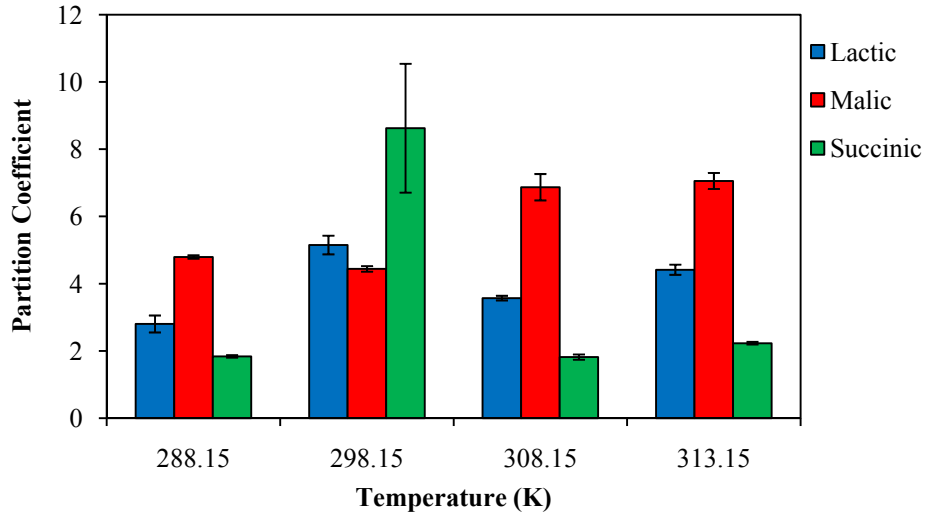


Figure 10. Effect of the anion bis(2,4,4-trimethylpenthyl)phosphinate on the partition coefficients of the studied acids with temperature, at a concentration of 0.50 M for L-lactic and L-malic acids and 0.05 M for succinic acid.

From the inspection of Figure 8, for all temperatures the extractability of the organic acid follows the trend succinic acid > L-malic acid > L-lactic acid, since succinic is the one that presents higher partition coefficients. This trend can be justified by the

hydrophilic character of each acid, since lactic acid is the smaller and more hydrophilic acid (water solubility of 86 wt% [9]) it presents more tendency to stay in the aqueous phase than to migrate to the ionic liquid phase. On the opposite end, the succinic acid is a larger compound and its solubility in water in only 6 wt% [60] which confirms its tendency to migrate to the ionic liquid phase. Despite the extra carboxylic group, malic acid presents a lower solubility in water (36 wt% [61]) than lactic acid, which makes it more easily extracted by hydrophobic ILs than lactic acid and less than succinic acid. This type of behavior was also seen by Matsumoto et al.[6] in the extraction of acetic, glycolic, propionic, lactic, pyruvic and butyric acids with imidazolium-based ILs.

In Figure 9, the extractions with $[P_{6\ 6\ 6\ 14}]$[Dec] presented similar partition coefficients for all the acids at all temperatures. The extraction with $[P_{6\,6\,6\,14}]$[Cl] presented higher partition coefficients than with $[P_{6\,6\,6\,14}]$[Dec], except for the L-lactic acid. In Figure 10, L-malic acid displays the highest partition coefficients. The results at 298 K show a completely different behavior from the rest and are not considered representative. The results obtained for both the $[P_{6\ 6\ 6\ 14}]$[Dec] and $[P_{6\ 6\ 6\ 14}]$[Phos] do not follow the water solubility trend found for $[P_{6\,6\,6\,14}]$[Cl]. This can be attributed to the ability of these two ILs to participate in hydrogen bonding, due to the presence of oxygen atoms with non bonding pairs of electrons. On the other hand, the presence of a pendent hydroxyl group in the L-malic acid will also enhance its ability to hydrogen bonding when compared to succinic acid. The same argument can be used for L-lactic acid which also presents an hydroxyl group.

3.2 Effect of Concentration on the Partition Coefficients

Tables 11, 12 and 13 and Figures 11, 12 and 13 report the values of the partition coefficients and the extraction efficiency obtained for L-lactic, L-malic and succinic acids, respectively, when each of the three phosphonium-based ILs were used at 298.15 K. For the L-lactic acid, both the partition coefficients and the extraction efficiency showed a slight increase with the increase in the acid concentration, as it can be concluded from Table 11 and Figure 11. The partition coefficients for $[P_{6\,6\,6\,14}]$[Cl] and $[P_{6\,6\,6\,14}]$[Dec] are all around 1 and 1.5 and the extraction efficiency is, in general, lower than 60 %. For the extractions with $[P_{6\,6\,6\,14}]$[Phos], the partition coefficients are higher than for the other two

ILs, presenting values between 2.1 and 5.2 and extraction efficiencies higher than 67 %. The extraction with this last IL presents a more marked effect of the L-lactic acid concentration that the other two studied ILs.

Table 11. Effect of the L-lactic acid concentration on the extraction efficiency at 298 K.

IL	Concentration (M)	Kp_2	Extraction Efficiency (%)
$[P_{6\,6\,6\,14}][Cl]$	0.05	1.39 ± 0.00	58.15
	0.10	1.52 ± 0.07	60.34
	0.20	1.59 ± 0.16	61.43
	0.50	1.64 ± 0.03	62.16
$[P_{6\,6\,6\,14}][Dec]$	0.05	1.44 ± 0.06	58.97
	0.10	1.52 ± 0.12	60.27
	0.20	1.61 ± 0.08	61.67
	0.50	1.95 ± 0.05	66.13
$[P_{6\,6\,6\,14}][Phos]$	0.05	2.07 ± 0.19	67.45
	0.10	2.32 ± 0.04	69.90
	0.20	4.00 ± 0.03	80.01
	0.50	5.15 ± 0.28	83.74

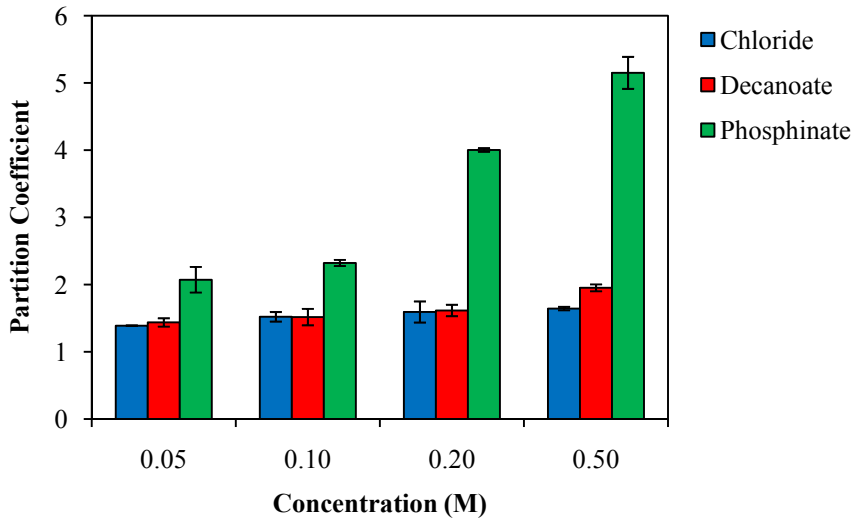


Figure 11. Effect of the L-lactic acid concentration on the partition coefficient at 298 K.

For the dicarboxylic acids (L-malic and succinic), the acid concentration effect is more marked than for the L-lactic acid. The change in the acid concentration can enhance two times the partition coefficients in the case of succinic acid. Nevertheless, for L-malic acid two distinct behaviors can be observed: while for the $[P_{6\,6\,6\,14}][Cl]$ and $[P_{6\,6\,6\,14}][Dec]$ the partition coefficients and extraction efficiencies were higher at lower concentrations, for the $[P_{6\,6\,6\,14}][Phos]$ this acid showed the same behavior as L-lactic acid, presenting the highest partition coefficient and extraction efficiency for more concentrated solutions. Table 12 and Figure 12 present the data obtained for L-malic acid, and Table 13 and Figure 13 the data for succinic acid.

Table 12. Effect of the L-malic acid concentration on the extraction efficiency at 298 K.

IL	Concentration (M)	Kp_2	Extraction Efficiency (%)
$[P_{6\,6\,6\,14}][Cl]$	0.05	5.21 ± 0.82	83.91
	0.10	3.09 ± 0.31	75.57
	0.20	3.06 ± 0.27	75.39
	0.50	1.59 ± 0.17	61.42
$[P_{6\,6\,6\,14}][Dec]$	0.05	4.01 ± 0.62	80.06
	0.10	1.93 ± 0.12	65.89
	0.20	1.11 ± 0.01	52.68
	0.50	2.35 ± 0.12	70.15
$[P_{6\,6\,6\,14}][Phos]$	0.05	1.49 ± 0.09	59.91
	0.10	1.43 ± 0.01	58.78
	0.20	1.57 ± 0.00	61.14
	0.50	4.44 ± 0.08	81.61

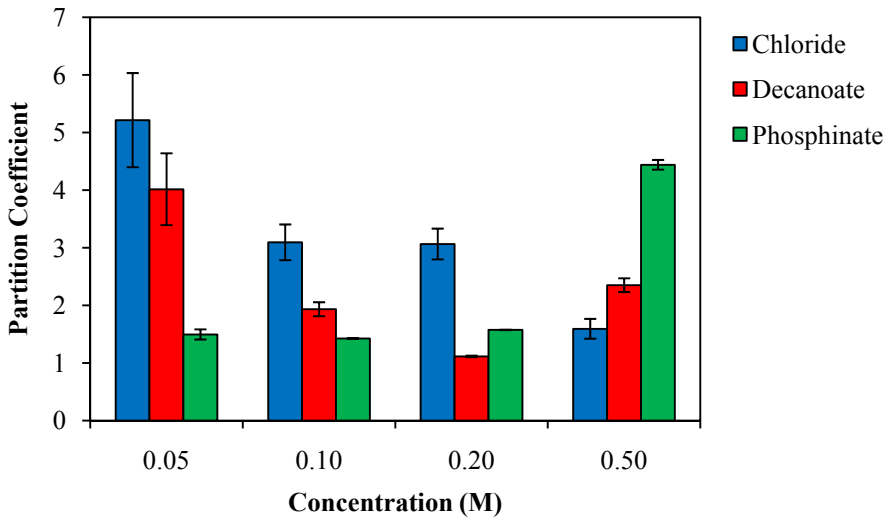


Figure 12. Effect of the L-malic acid concentration on the partition coefficients at 298 K.

For the L-malic acid, it is interesting to observe that when $[P_{6\,6\,6\,14}]$[Dec] is used stable micelles are formed (Table 6). In this case, although almost no L-malic acid is left in the aqueous phase, a large amount could not be accounted for, which indicates that it is probably in the spongy interface. For the other two ILs no interface was observed and two scenarios were identified: for the $[P_{6\,6\,6\,14}]$[Cl] the mass balance almost closes, but a large amount of L-malic acid remained in the aqueous phase, while for the $[P_{6\,6\,6\,14}]$[Phos] almost all the acid was extracted from the aqueous phase, but the mass balance does not close.

Table 13. Effect of the succinic acid concentration on the extraction efficiency at 289 K.

IL	Concentration (M)	Kp_2	Extraction Efficiency (%)
$[P_{6\,6\,6\,14}][Cl]$	0.05	8.52 ± 1.74	89.49
	0.10	6.44 ± 0.59	86.55
	0.20	6.10 ± 0.52	85.91
	0.50	4.33 ± 0.09	81.25
$[P_{6\,6\,6\,14}][Dec]$	0.05	4.19 ± 0.39	80.75
	0.10	2.87 ± 0.05	74.14
	0.20	2.75 ± 0.12	73.35
	0.50	3.38 ± 0.13	77.18
$[P_{6\,6\,6\,14}][Phos]$	0.05	8.62 ± 1.92	89.61
	0.10	4.24 ± 0.21	80.90
	0.20	3.55 ± 0.08	78.00
	0.50	5.01 ± 0.28	83.35

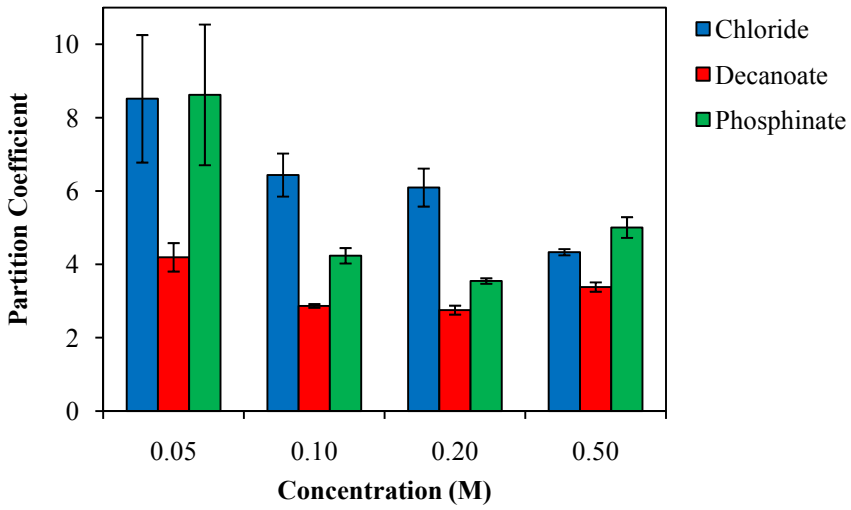


Figure 13. Effect of the succinic acid concentration on the partition coefficients at 298 K.

The partition coefficients for L-malic and succinic are in general larger than those for L-lactic acid. For both L-malic and succinic acid, the lowest concentration of acid tested was the one that yielded the best results. Nevertheless, the results obtained for the extractions of L-malic acid with the IL $[P_{6\,6\,6\,14}]$[Phos] were quite unexpected since they do not follow the trend obtained for the other two ILs also studied.

3.3 Effect of Temperature on the Partition Coefficients

For the study of the effect of temperature in the extraction efficiency and the partition coefficients of the acids, the concentration was kept constant. For each acid, the concentration which yielded the highest partition coefficient and also higher extraction efficiency was selected, which means that for the L-lactic acid 0.50 M was used while for the other two acids the concentration of 0.05 M was used. Four temperatures were studied, 288.15, 298.15, 308.15 and 313.15 K. Table 14 and Figure 14 report the effect of temperature in the extraction efficiency of L-lactic acid using the three ILs. In general, the temperature does not have a significant effect in the extractions for $[P_{6\,6\,6\,14}]$[Cl] and for the other two ILs there is only a slight variation in the partition coefficients with temperature. For the IL $[P_{6\,6\,6\,14}]$[Dec] an increase in the partition coefficients is observed, while for the IL $[P_{6\,6\,6\,14}]$[Phos] the partition coefficients show a slight decrease with temperature.

Table 14. Effect of temperature on the L-lactic acid partition coefficient and extraction efficiency using an initial concentration of acid of 0.50 M.

IL	Temperature (K)	Kp_2	Extraction Efficiency (%)
$[P_{6\,6\,6\,14}][Cl]$	288.15	1.53 ± 0.04	60.44
	298.15	1.64 ± 0.03	62.16
	308.15	1.55 ± 0.06	60.72
	313.15	1.24 ± 0.08	55.36
$[P_{6\,6\,6\,14}][Dec]$	288.15	2.50 ± 0.06	71.45
	298.15	1.95 ± 0.05	66.13
	308.15	3.11 ± 0.13	75.69
	313.15	2.10 ± 0.04	67.71
$[P_{6\,6\,6\,14}][Phos]$	288.15	2.80 ± 0.25	73.69
	298.15	5.15 ± 0.28	83.74
	308.15	3.57 ± 0.07	78.12
	313.15	4.41 ± 0.15	81.53

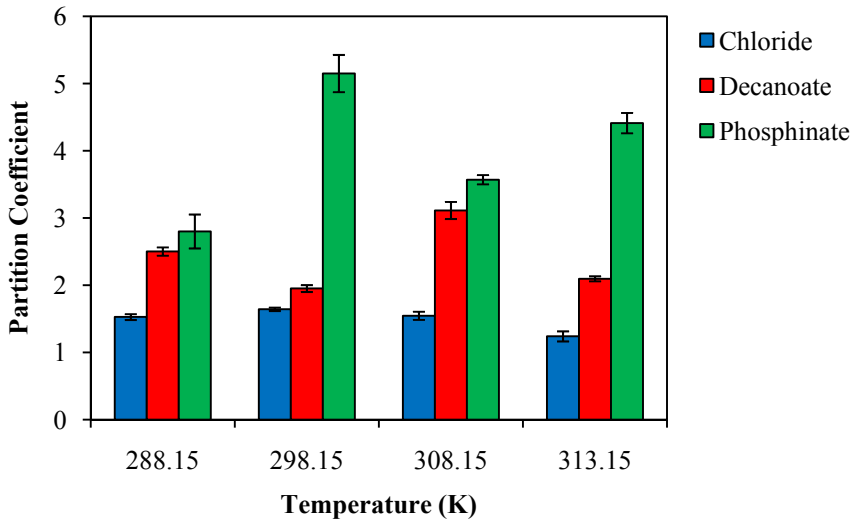


Figure 14. Effect of temperature on the L-lactic acid partition coefficient at a concentration of 0.50 M.

For L-malic acid, the extractions for $[P_{6\,6\,6\,14}]$[Phos] were performed at an higher concentration (0.50 M) than for the other ILs (0.05 M), since this was the concentration where the highest efficiency was achieved. The same behavior can be observed for the ILs $[P_{6\,6\,6\,14}]$[Cl] and $[P_{6\,6\,6\,14}]$[Dec], where the partition coefficients slightly decrease with temperature, while for the IL $[P_{6\,6\,6\,14}]$[Phos] the partition coefficients showed an small increase with the temperature. The data regarding the L-malic acid is displayed in Table 15 and Figure 15.

Table 15. Effect of temperature on the L-malic acid partition coefficient and extraction efficiency using an initial concentration of acid of 0.05 M for $[P_{6\,6\,6\,14}]$[Cl] and $[P_{6\,6\,6\,14}]$[Dec], and of 0.50 M for $[P_{6\,6\,6\,14}]$[Phos].

IL	Temperature (K)	Kp_2	Extraction Efficiency (%)
$[P_{6\,6\,6\,14}]$[Cl]	288.15	2.97 ± 0.16	74.81
	298.15	5.21 ± 0.82	83.91
	308.15	4.93 ± 0.39	83.14
	313.15	2.66 ± 0.41	72.64
$[P_{6\,6\,6\,14}]$[Dec]	288.15	2.47 ± 0.26	71.17
	298.15	4.01 ± 0.62	80.06
	308.15	2.62 ± 0.36	72.41
	313.15	1.59 ± 0.16	61.42
$[P_{6\,6\,6\,14}]$[Phos]	288.15	4.79 ± 0.05	82.73
	298.15	4.44 ± 0.08	81.61
	308.15	6.87 ± 0.39	87.29
	313.15	7.06 ± 0.24	87.59

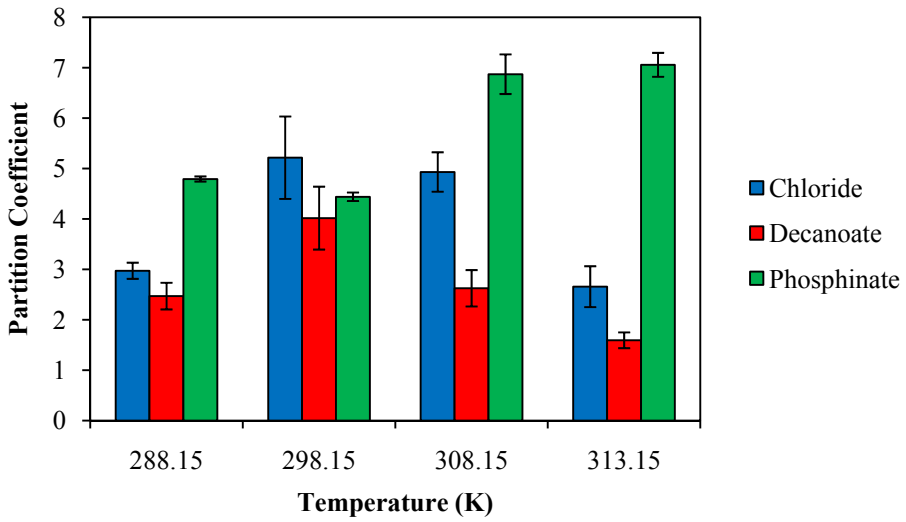


Figure 15. Effect of temperature on the L-malic acid partition coefficients at a concentration of 0.50 M for $[P_{6\,6\,6\,14}][Phos]$ and 0.05 M for $[P_{6\,6\,6\,14}][Cl]$ and $[P_{6\,6\,6\,14}][Dec]$.

Table 16 and Figure 16 report the data obtained for the effect of temperature in the succinic acid partition coefficient and extraction efficiency. For this acid these extractions were carried out at 0.05 M and those using $[P_{6\,6\,6\,14}][Cl]$ and $[P_{6\,6\,6\,14}][Phos]$ ILs were the most affected by temperature.

Table 16. Effect of temperature on the succinic acid partition coefficient and extraction efficiency using an initial concentration of acid of 0.05 M.

IL	Temperature (K)	Kp_2	Extraction Efficiency (%)
$[P_{6\,6\,6\,14}][Cl]$	288.15	2.81 ± 0.35	73.75
	298.15	8.52 ± 1.74	89.49
	308.15	8.15 ± 1.47	89.07
	313.15	3.65 ± 0.59	78.48
$[P_{6\,6\,6\,14}][Dec]$	288.15	1.85 ± 0.15	64.92
	298.15	4.19 ± 0.39	80.75
	308.15	3.48 ± 0.17	77.69
	313.15	1.74 ± 0.05	63.50
$[P_{6\,6\,6\,14}][Phos]$	288.15	1.84 ± 0.04	64.74
	298.15	8.62 ± 1.92	89.61
	308.15	1.82 ± 0.08	64.48
	313.15	2.23 ± 0.04	69.03

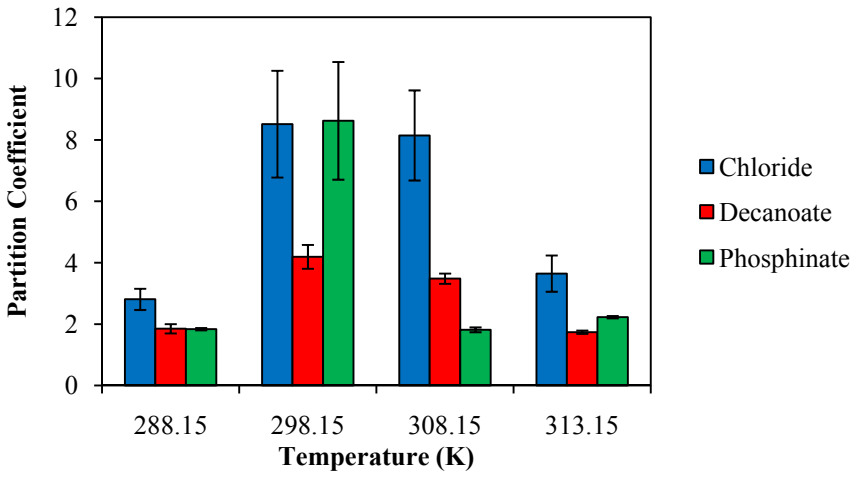


Figure 16. Effect of temperature on the succinic acid partition coefficient at a concentration of 0.05 M.

3.4 Multistep extraction

In order to access if the non-quantified fraction of the acids was in fact retained in the spongy phase, a multi-step extraction was carried out where the IL phase was removed, and pure IL was added to the aqueous phase together with the interface. The IL [$P_{6\,6\,6\,14}$][Dec] was chosen to perform this multi-step extraction since it presented the highest losses for all acids. This procedure was done at 298 K for all the acids at the concentration of 0.50 M, by removing the ionic liquid phase of the extraction and adding more pure IL (*circa* 0.4 g) to the remaining interface and aqueous phase. Then, the same procedure of the extractions was carried out. This step proved that in fact some acid was inside the micelles in the spongy phase. Table 17 presents the results of the multistep done, where $Conc_{IL2}$ and $Conc_{AQ2}$ represent the concentration quantified in the ionic liquid phase and in the aqueous phase after the multistep, respectively.

Table 17. Results from the multistep extraction with [$P_{6\,6\,6\,14}$][Dec] for the three acids studied in this work at 298 K.

Compound	$Conc_{i0}$ (g/g) × 10^3	$Conc_{AQ}$ (g/g) × 10^3	$Conc_{NQ}$ (g/g) × 10^3	$Conc_{IL2}$ (g/g) × 10^3	$Conc_{AQ2}$ (g/g) × 10^3	EE (%)
L-Lactic Acid	45.20	1.21 ± 0.00	14.10	14.94 ± 0.39	2.13 ± 0.02	97
L-Malic Acid	67.26	0.11 ± 0.01	19.97	12.89 ± 0.42	1.48 ± 0.07	64
Succinic Acid	59.27	0.14 ± 0.01	13.38	8.41 ± 0.32	–	62

In the multistep extraction, the formation of an interface did not occur for any acid. In the extraction of succinic acid the final volume of aqueous phase was very small, and so the quantification was not possible. For the L-lactic acid, 97 % of the acid that remained in the aqueous phase and in the interface was extracted to the ionic liquid phase, in the case of L-malic acid 64 % and for succinic acid only 62 %. Table 18 reports the partition coefficients and extraction efficiencies for the three acids after the multistep extraction and Figure 17 compares the partition coefficients calculated after one and two extraction steps.

Table 18. Partition coefficients and extraction efficiencies for single and multistep extraction with $[P_{6\,6\,6\,14}][Dec]$ for the three acids studied in this work at 298 K.

Compound	Kp_2 for one step	Kp_2 for two steps	EE for one step (%)	EE for two steps (%)
L-Lactic Acid	1.95 ± 0.05	18.62 ± 0.09	66.13	99.18
L-Malic Acid	2.35 ± 0.12	7.31 ± 0.16	70.15	89.32
Succinic Acid	3.38 ± 0.13	10.60 ± 0.17	77.18	91.38

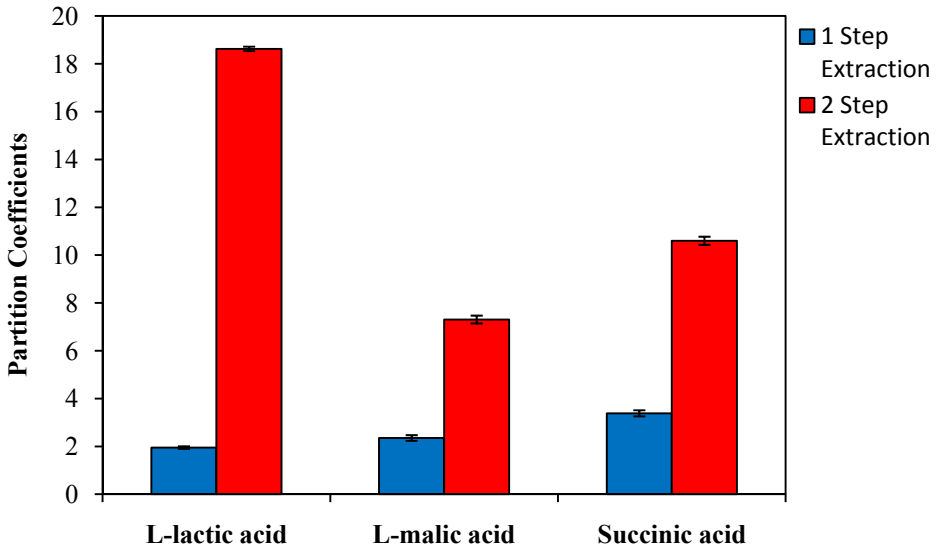


Figure 17. Partition Coefficients for the one and two steps extractions of the studied acids, at 298 K with $[P_{6\,6\,6\,14}][Dec]$.

As Table 18 and Figure 17 reports, the partition coefficients of the acids show a great increase when a second extraction step is performed. This increase in the partition coefficients and extraction efficiencies proves that a great amount of acid, which was not quantified in the first step of the extraction, was indeed retained in the spongy interface. With the second extraction step no interface was observed and more acid was extracted and quantified in the ionic liquid phase, in all the cases. Nevertheless, even in the absence of interface in the system, there are still some extractions where the full amount of acid is not quantified. Martak et al.[41-42, 46] also studied the extraction of L-lactic acid with phosphonium-based ILs. These authors proposed the formation of complexes between the

IL, the acid and the water. The formation of these complexes could explain the errors in the quantification of the acids since in this work only the acid in the free from was determined.

3.5 Recovery step

In this work, it was proved that ILs can efficiently extract small chain acids like L-lactic, L-malic and succinic acid from aqueous solutions. However, after the extraction process there is a need to recover these acids from the IL. For this purpose, two processes were tested to recover the extracted acid, micro-distillation and stripping with a strong base.

The micro-distillation was performed in vacuum due to the high boiling temperatures of the acids. For the distillation of L-lactic acid it was used a vacuum of 0.006 atm and the temperature was raised until 403 K. L-lactic acid has a boiling temperature of 395 K at 0.02 atm, L-malic and succinic acids have decomposition temperatures at 423 and 508 K, at atmospheric pressure, respectively. For the distillation of both L-malic and succinic acids, a lower vacuum was used (0.5 atm) and the temperature was raised until 393 and 423 K, respectively. Distillate was only recovered in the distillation of L-malic acid. However, the amount was too small to be quantified; instead, the ionic liquid phase used for the distillation was quantified before and after the distillation to verify if the acids were extracted from the IL. The quantification of the acid in the IL phase used in the distillation showed no significant change in its concentration before and after the distillation. Thus, it is not possible to recover the studied acids via distillation.

For the stripping of the acid from the IL, solid sodium hydroxide (NaOH) was used. The NaOH was added directly to the IL phase and the same procedure of the extractions was carried out. The addition of the NaOH promotes the formation of acid in the dissociated form and thus its solubilization in the aqueous phase.

After the centrifugation step two phases can be distinguish, an ionic liquid phase and an aqueous phase. Due to the reduce volume of the formed aqueous phase, only the ionic liquid phase was quantified. The amount of NaOH initially added was in the proportion of 1:1 in mass to the acid in the IL phase. The results showed that the only 36 %

in mass of the acid was recovered from the IL phase. Nevertheless, when more NaOH was added to the IL phase, more acid was recovered reaching 73 % in mass of acid recovered.

3.6 COSMO-RS

As it was mentioned in the introduction, the high number of possible combinations of anions and cations is usually seen as an advantage of using ILs, since it allows the design of task specific ILs. However, in order to determine the suitability of an IL for a certain process, a large number of trial test are usually needed. The use of simulation tools can be very useful in solving this problem, since they allow performing this a priori screening in a fast and inexpensive way. The main drawback is the availability and the reliability of these predictive tools and the amount of information needed.[62-63]

The COSMO-RS (Conductor-Like Screening Model for Real Solvents) is a method used for the prediction of phase equilibria and bulk properties of pure fluids and mixtures based on unimolecular quantum calculations. This method has already been successfully used to describe the binary liquid-liquid equilibria of ILs and alcohols, hydrocarbons, ethers, ketones, and water systems.[37, 64] The COSMO-RS proved to be an a priori model capable of predicting in a qualitative way the phase equilibria behavior between water and imidazolium-, pyridinium-, piperidinium-, pyrrolidinium- and phosphonium-based ILs.[44, 65-67]

In this work, the feasibility of using COSMO-RS to predict the LLE of ternary systems containing water, IL ([$P_{6\,6\,6\,14}$][Cl] and [$P_{6\,6\,6\,14}$][Dec]) and acid (L-lactic, L-malic and succinic) was evaluated. In the approach followed when using COSMO-RS the formation of micelles was not taken into account. The composition of the two liquid phases in equilibrium was compared to the composition experimentally obtained after the centrifugation step. The binary systems containing water + acid and IL + acid were not presented since the predictions obtained with COSMO-RS were not accurate. Also, COSMO-RS was not able to predict any LLE points bellow 0.1 wt % of acid.

Higher deviations from the experimental data were obtained for [$P_{6\,6\,6\,14}$][Cl] than for [$P_{6\,6\,6\,14}$][Dec]. This difference was also observed by Freire et al.[44]. The obtained results indicate that COSMO-RS takes the chloride anion as more hydrophilic than the decanoate anion, while experimental data indicates the opposite. Freire et al.[44] addressed this problem

to the fact that the chloride anion presents a higher charge density due to its smaller size, allowing therefore stronger Coulombic interactions, which is probably not taken into account in COSMO-RS. Nevertheless, for all the studied systems it can be seen that the slope of the tie-lines changes with the concentration of acid, showing positive slopes for small concentrations of acid, thus indicating the favorable extraction of the acid to the ionic liquid phase. According to the these figures, the smaller the acid concentration, the steeper the tie-lines will be, and higher extraction efficiencies will be achieved.

Figures 18, 19 and 20 report the phase behavior predicted using COSMO-RS for the ternary systems composed of $[P_{6\ 6\ 6\ 14}][Dec]$ and water and L-lactic, L-malic and succinic acids respectively. For the systems containing L-malic and succinic acid higher slopes than for the system containing L-lactic acid were found. This indicates that $[P_{6\,6\,6\,14}]$ [Dec] at 298 K extracts more L-malic and succinic acid than L-lactic acid, which is consistent with the data presented in this work.

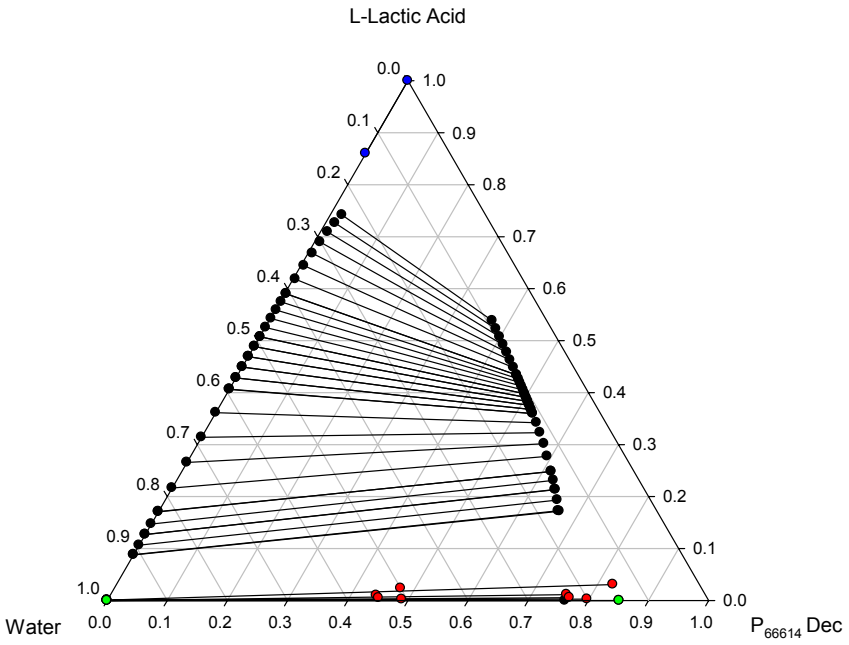


Figure 18. Predicted phase behavior for the $[P_{6\,6\,6\,14}][Dec]$ + L-lactic acid + water ternary system at 295 K (in wt %) using COSMO-RS (—●—), experimental data from this work (—●—) and experimental data for binary systems (—●—)[44](—●—)[9].

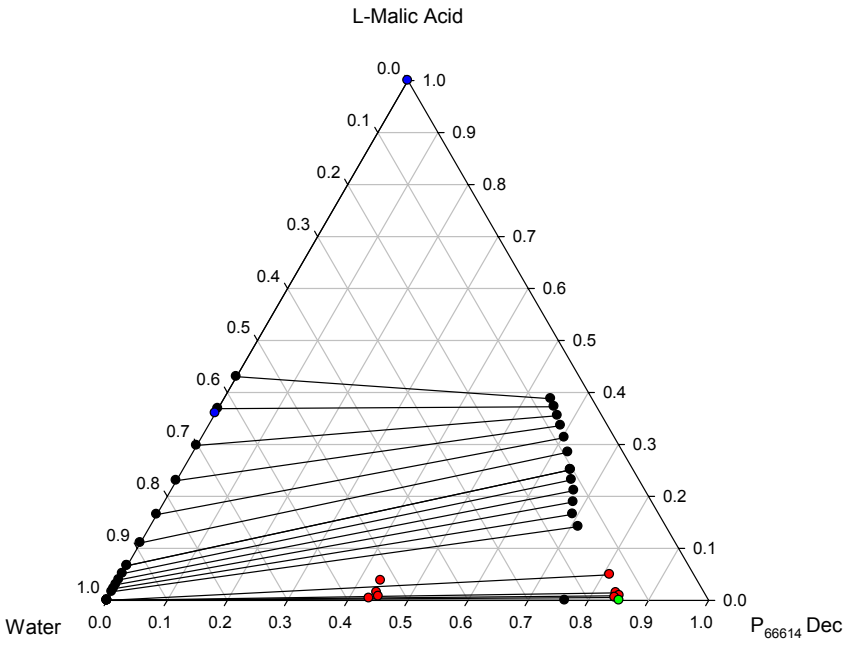


Figure 19. Predicted phase behavior for the $[P_{6\,6\,6\,14}][Dec]$ + L-malic acid + water ternary system at 295 K (in wt %) using COSMO-RS (—●—), experimental data from this work (—●—) and experimental data for binary systems (—●—)[44](—●—)[61].

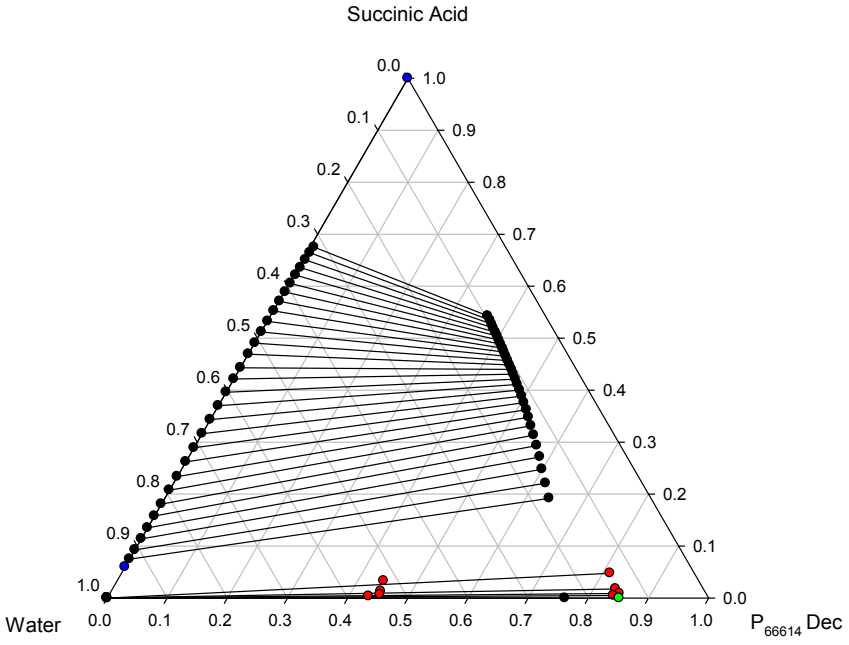


Figure 20. Predicted phase behavior for the $[P_{6\,6\,6\,14}][Dec]$ + succinic acid + water ternary system at 295 K (in wt %) using COSMO-RS (—●—), experimental data from this work (—●—) and experimental data for binary systems (—●—)[44] (—●—)[60].

In Figures 21, 22 and 23 the LLE phase behavior predicted using COSMO-RS for $[P_{6\ 6\ 6\ 14}][Cl]$ and water and L-lactic, L-malic and succinic acids, respectively, are presented. When comparing the ternary systems $[P_{6\ 6\ 6\ 14}][Dec]$ + water + acid with the $[P_{6\ 6\ 6\ 14}][Cl]$ + water + acid, the first showed higher slopes of the tie lines implying that $[P_{6\ 6\ 6\ 14}][Dec]$ has a higher extractant ability than $[P_{6\ 6\ 6\ 14}][Cl]$ at 298 K, which the experimental data showed after the second extraction step. However, analyzing the COSMO-RS predictions for extraction of the different acid using $[P_{6\ 6\ 6\ 14}][Cl]$, L-malic acid presents higher concentrations in the IL phase, which is not in agreement with the obtained experimental data.

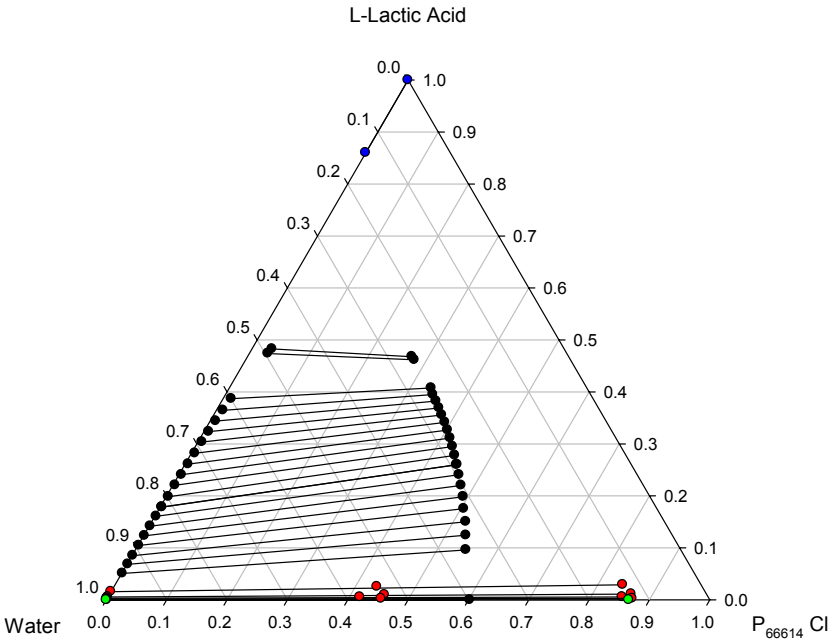


Figure 21. Predicted phase behavior for the $[P_{6\ 6\ 6\ 14}][Cl]$ + L-lactic acid + water ternary system at 295 K (in wt %) using COSMO-RS (—●—), experimental data from this work (—●—) and experimental data for binary systems (—●—)[44](—●—)[9].

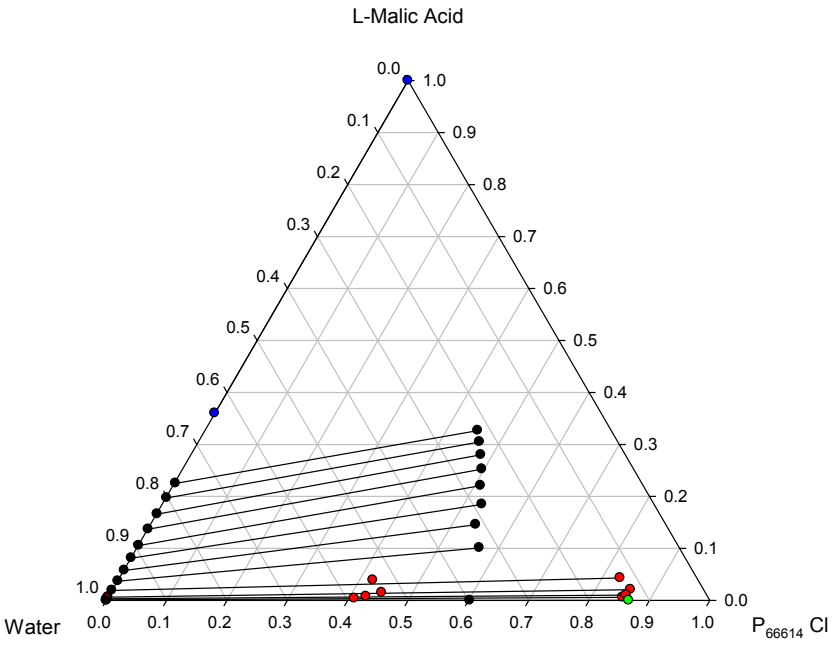


Figure 22. Predicted phase behavior for the $[P_{6\,6\,6\,14}][Cl]$ + L-malic acid + water ternary system at 295 K (in wt %) using COSMO-RS (—◆—), experimental data from this work (—◆—) and experimental data for binary systems (—◆—)[44](—◆—)[61].

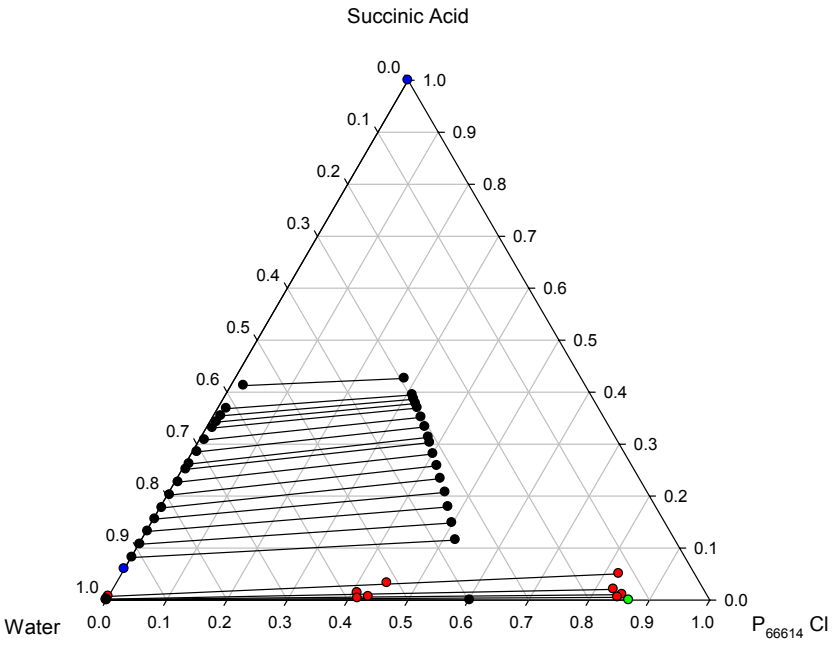


Figure 23. Predicted phase behavior for the $[P_{6\,6\,6\,14}][Cl]$ + succinic acid + water ternary system at 295 K (in wt %) using COSMO-RS (—◆—), experimental data from this work (—◆—) and experimental data for binary systems (—◆—)[44] (—◆—)[60].

4 CONCLUSIONS

The first conclusion that can be taken from the present work is that phosphonium-based ILs are better extractants than the organic solvents traditionally used. The partition coefficients for organic compounds are usually close to 1 [8, 14] while the partition coefficients obtained in this work are between 1.11 and 8.62. To be mentioned that in the literature, most of the times the quantification of the acid in the IL phase is not performed and it is assumed that all the acid that is not in the aqueous phase was recovered. This leads to incorrect evaluation of the amount of the acid extracted and to an artificial increase of the partition coefficients and the extraction efficiencies.

Another important conclusion is that different mechanisms of extraction of the acid might occur, namely through reverse micelles and the formation of complexes between the acid, the IL and water. In certain cases, the micelles formed are too stable and cannot be efficiently broken. This leads to losses in the amount of the acid extracted. However, the proposed multistep procedure proved to be efficient in breaking the spongy phase formed since after the second extraction step, this third phase does not form. Nevertheless, in some cases it was observed that although the spongy phase was not formed the acid material balance was not attained probably indicating the formation of complexes containing acid.

The extraction efficiency of the three ILs showed different behaviors regarding the studied acids. For the L-lactic acid extraction, the IL that showed the best extraction performance was $[P_{6\,6\,6\,14}][Phos]$; for the extraction of succinic acid, the highest partition coefficients were obtained for the $[P_{6\,6\,6\,14}][Cl]$ and $[P_{6\,6\,6\,14}][Phos]$ ILs; for L-malic acid all ILs presented similar partition coefficients. However, if the multistep extraction is considered, the partition coefficients for all acid are greatly increased with L-lactic acid showing a partition coefficient ten times higher, while L-malic and succinic acid showed a partition coefficient three times higher than when only one extraction step is used.

From the other two variables analyzed, the concentration of the acid in the starting solution and the temperature of the process, the first proved to have a great effect on the partition coefficients, while the second only has a marginal effect. The extraction of L-lactic acid was more efficient at higher concentrations of the starting solution (0.50 M) while L-malic and succinic acid proved to be more easily extracted at lower ones (0.05 M).

Two recovery processes were attempted: a low-pressure distillation and pH variation. The first one seemed to be the most promising since ILs present negligible vapor

pressure, which would allow the extracted acid to be separated from the ionic liquid, and the recovery of the IL for reuse. However, this process wasn't effective and the acid recovery was not possible. The pH variation was done by addition of solid NaOH and it proved to efficiently strip the acid from the IL with the recovery of 73 % in mass of the extracted acid.

The COSMO-RS predictive ability was evaluated through the comparison with the experimental results. This method seems to be a good qualitative predictive tool for these systems. However, it needs to be used with care since large differences between the data obtained and the experimental data were found, especially for the chloride anion.

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APPENDIX A

A1. ^{1}H, ^{13}C and ^{19}F NMR spectra for $[P_{6\,6\,6\,14}][Cl]$

The ^{1}H, ^{13}C and ^{19}F NMR spectra of $[P_{6\,6\,6\,14}][Cl]$ were obtained with a Brucker Advance II + 400 MHz equipment in $CDCl_3$ are presented in Figures A1, A2 and A3 respectively.

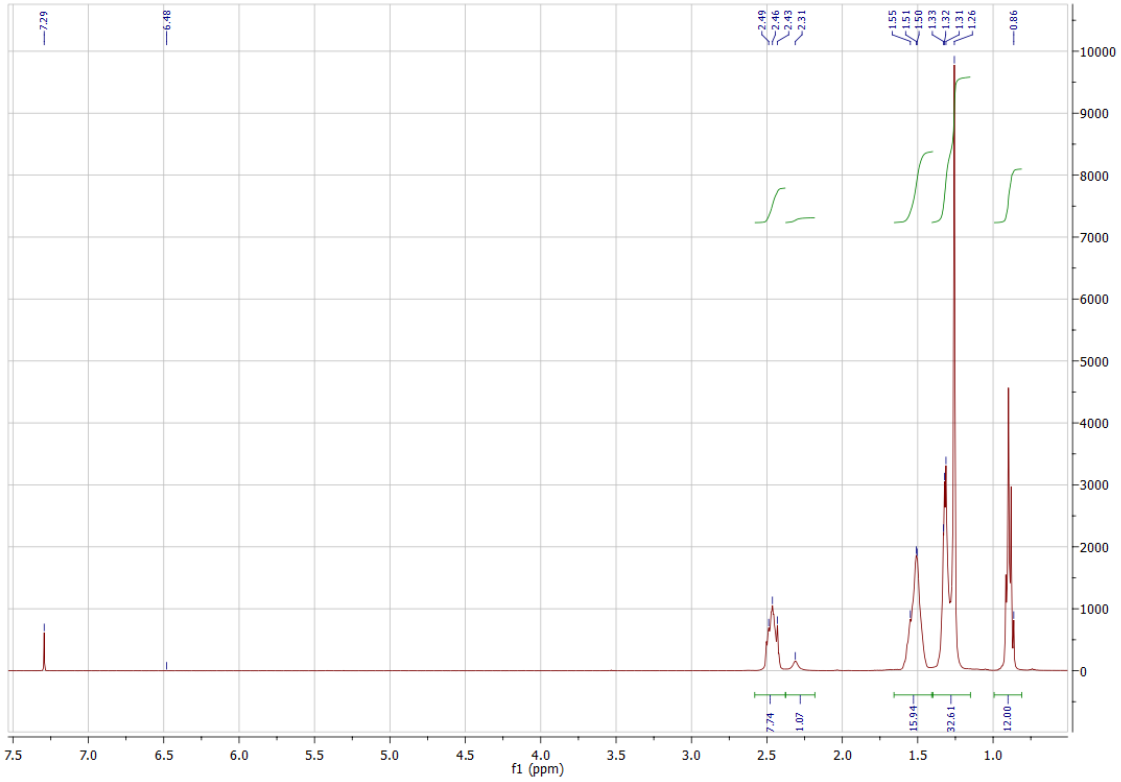

Figure A1. ^{1}H NMR spectra of $[P_{6\,6\,6\,14}][Cl]$.

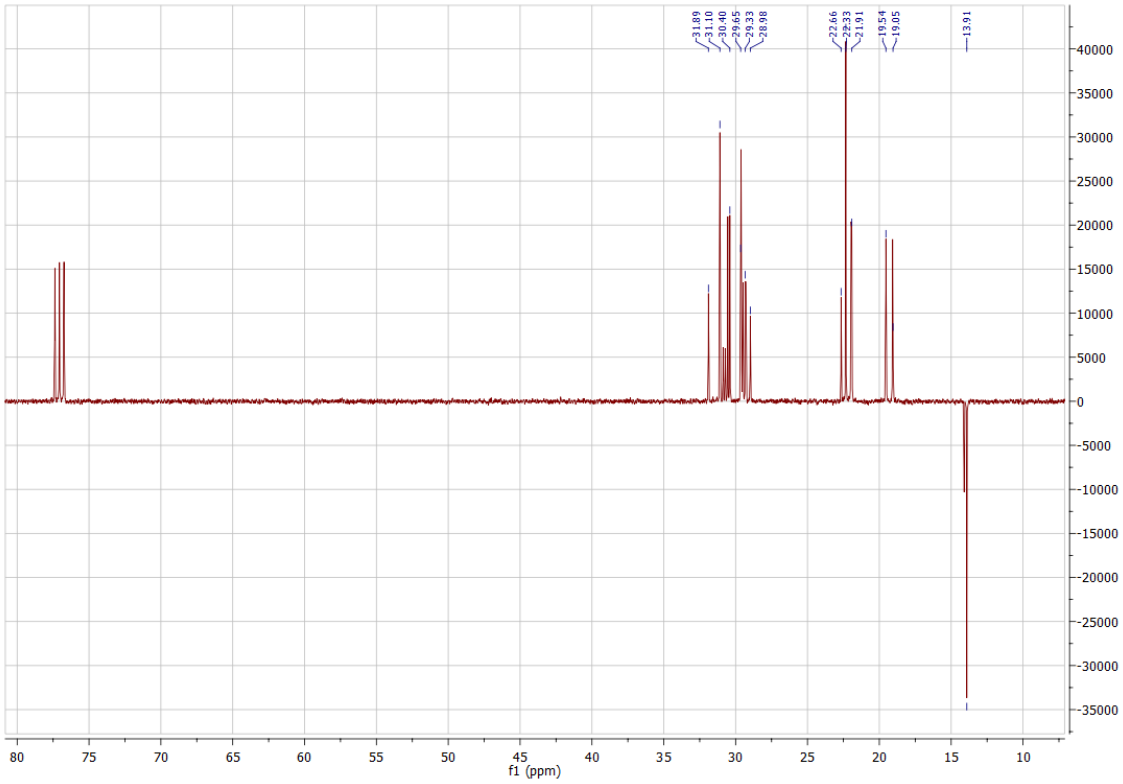

Figure A2. ^{13}C NMR spectra of $[P_{6\,6\,6\,14}][Cl]$.

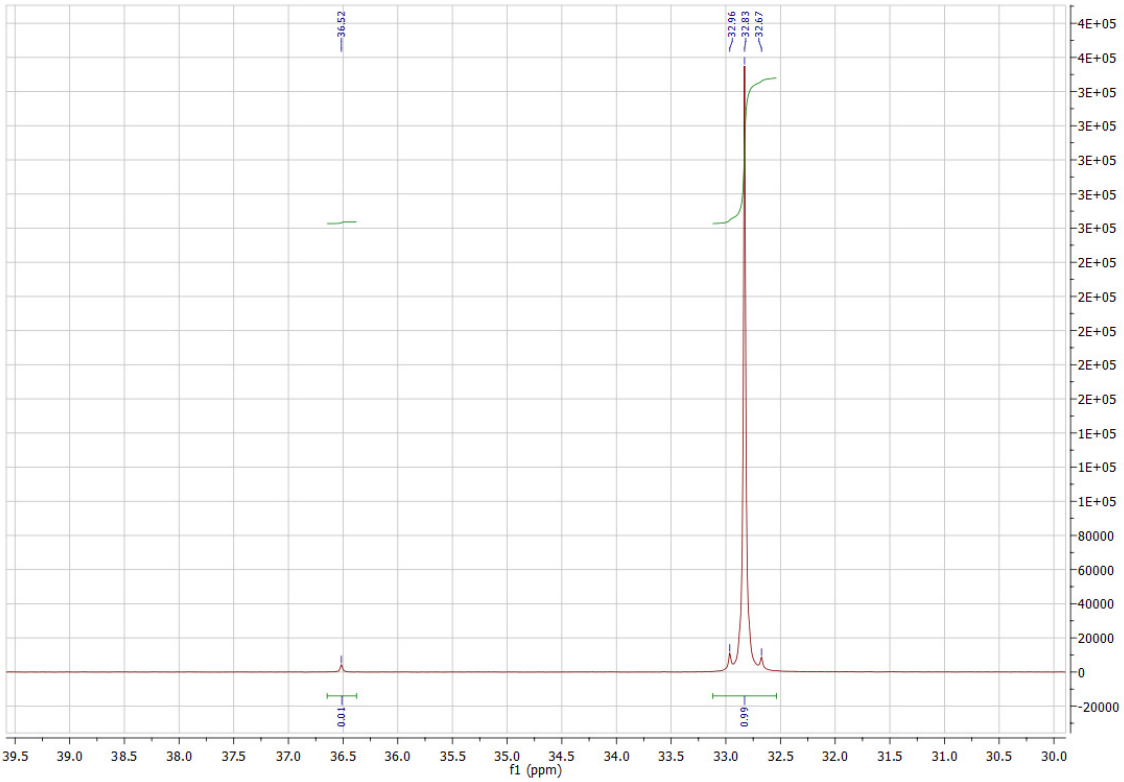

Figure A3. ^{19}F NMR spectra of $[P_{6\,6\,6\,14}][Cl]$.

A2. ^{1}H, ^{13}C and ^{19}F NMR spectra for $[P_{6\,6\,6\,14}][Dec]$

The ^{1}H, ^{13}C and ^{19}F NMR spectra of $[P_{6\,6\,6\,14}][Dec]$ were obtained with a Brucker Advance II + 400 MHz equipment in $CDCl_3$ are presented in Figures A4, A5 and A6 respectively.

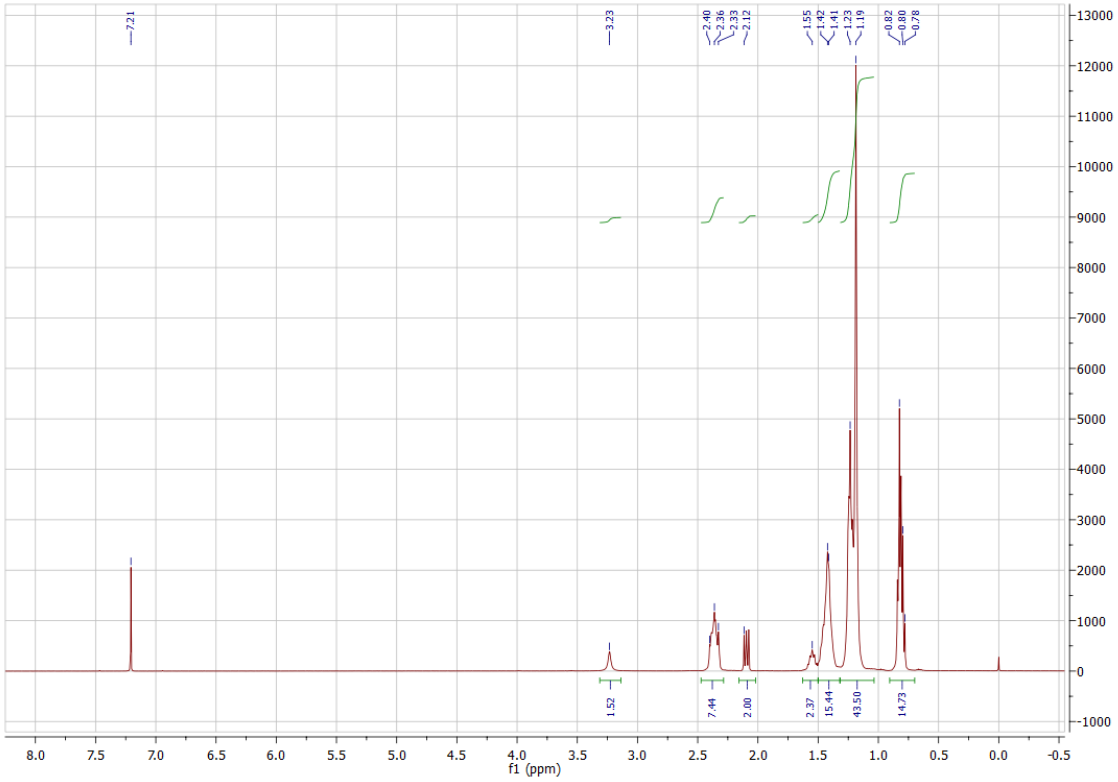

Figure A4. ^{1}H NMR spectra of $[P_{6\,6\,6\,14}][Dec]$.

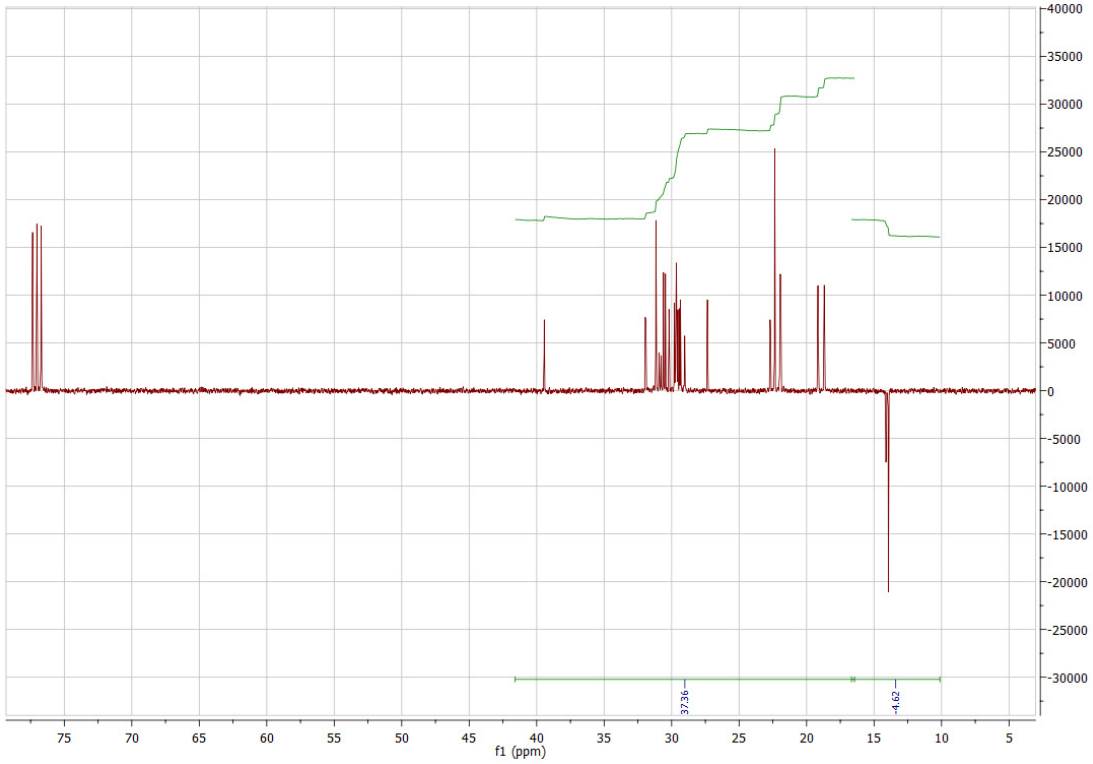

Figure A5. ^{13}C NMR spectra of $[P_{6\,6\,6\,14}][Dec]$.

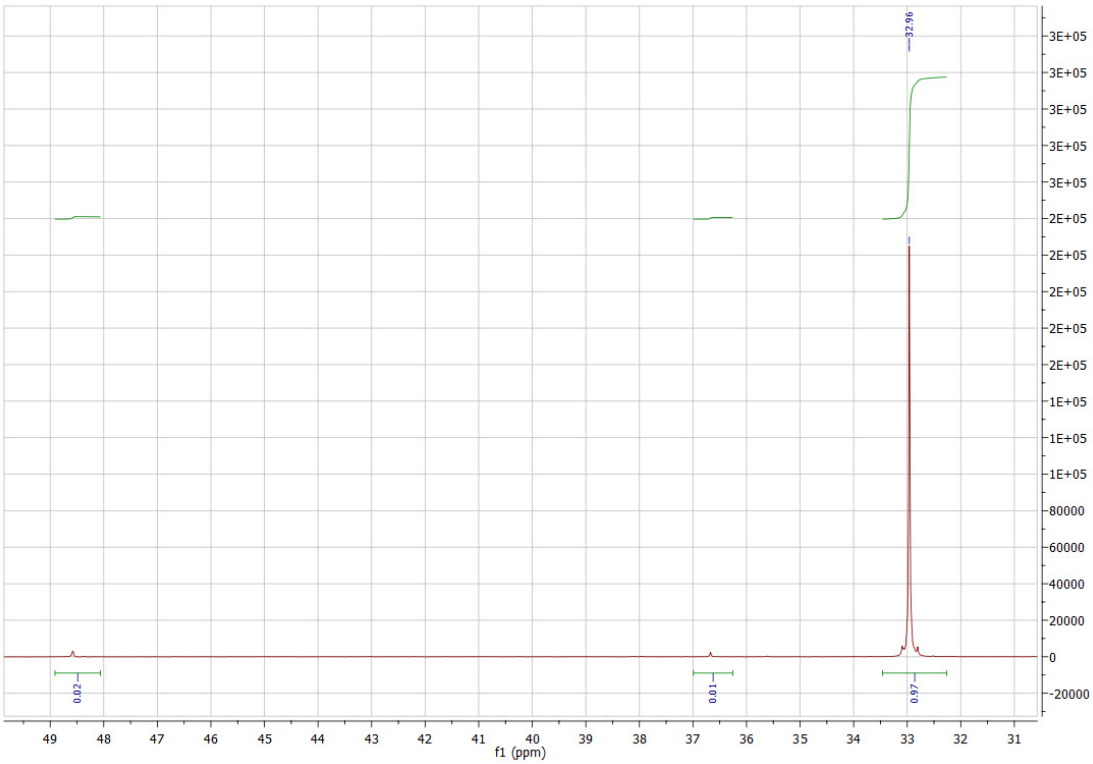

Figure A6. ^{19}F NMR spectra of $[P_{6\,6\,6\,14}][Dec]$.

A3. ^{1}H, ^{13}C and ^{19}F NMR spectra for $[P_{6\,6\,6\,14}][Phos]$

The ^{1}H, ^{13}C and ^{19}F NMR spectra of $[P_{6\,6\,6\,14}][Phos]$ were obtained with a Brucker Advance + 300 MHz equipment in DMSO are presented in Figures A7, A8 and A9 respectively.

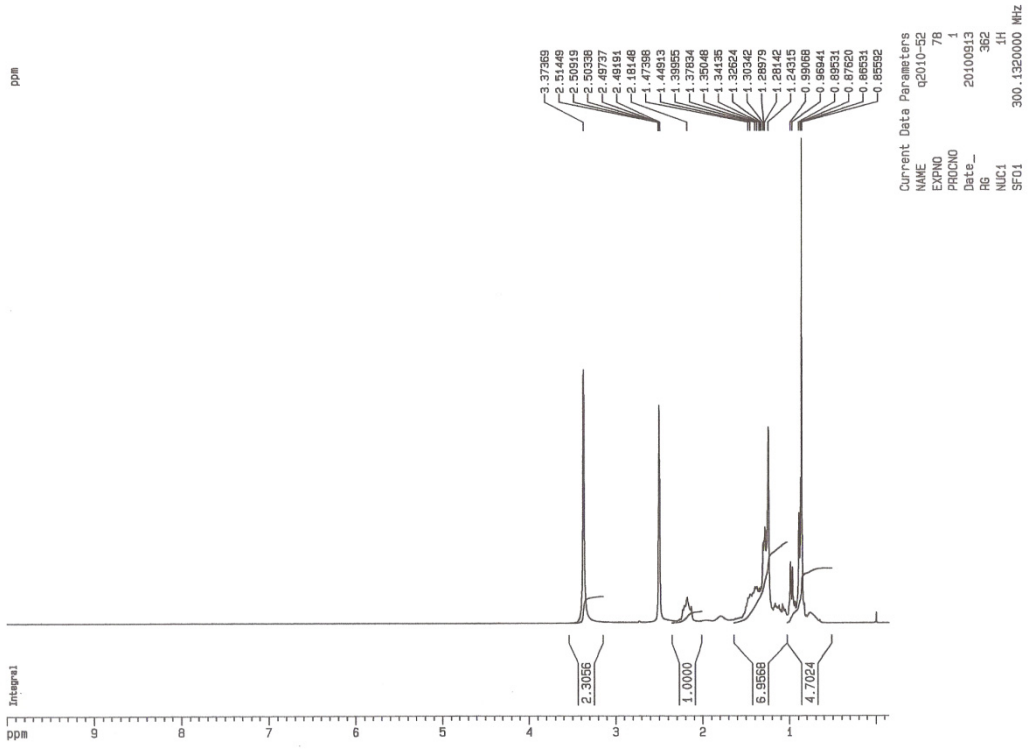

Figure A7. ^{1}H NMR spectra of $[P_{6\,6\,6\,14}][Phos]$.

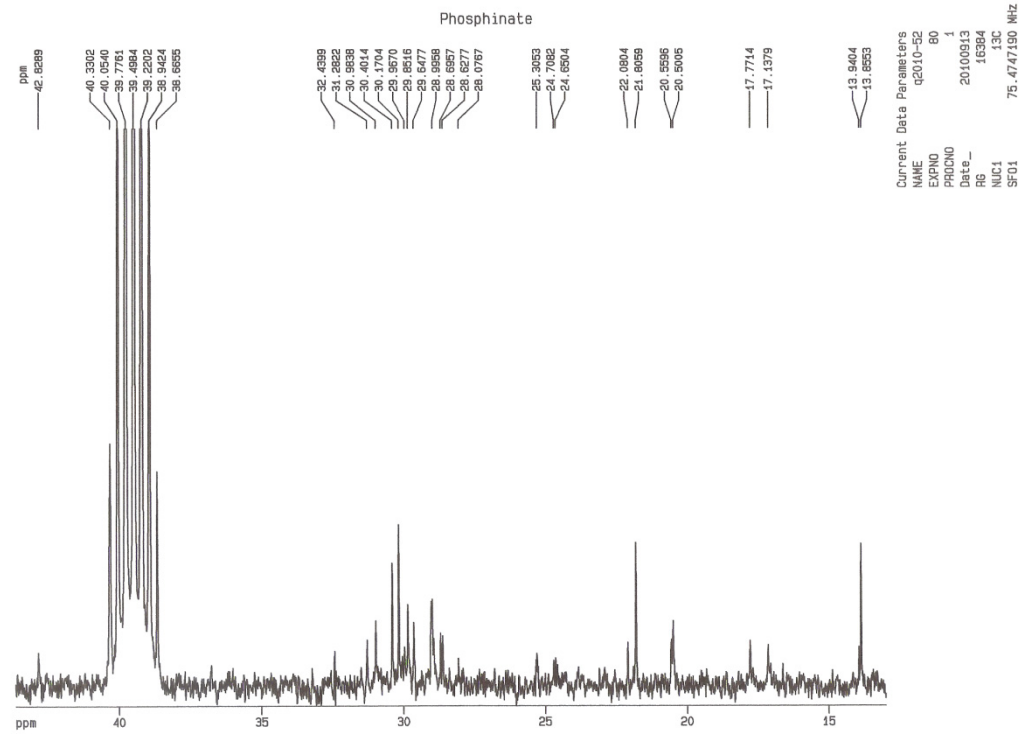

Figure A8. ^{13}C NMR spectra of $[P_{6\,6\,6\,14}]$[Phos].

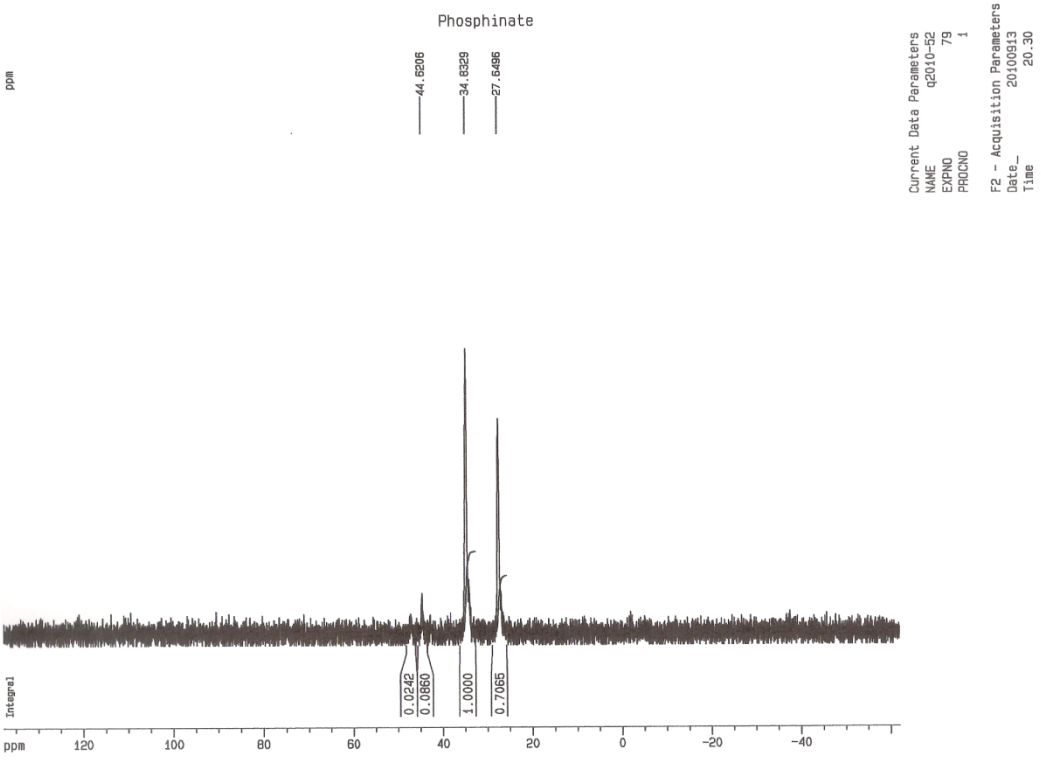

Figure A8. ^{19}F NMR spectra of $[P_{6\,6\,6\,14}]$[Phos].

APPENDIX B

B1. Calibration curve for L-lactic acid

In order to determine the amount of L-lactic acid in each phase, a calibration curve was used. For this purpose, nine standards of different known concentrations of L-lactic acid were prepared in water. Table B1 presents the concentration of the prepared standards in M and in g of solute/g of solution and the respective average area of the picks acquired. Figure B1 presents the calibration curve obtained and respective slope and correlation coefficient.

Table B1. L-lactic acid standards and respective area.

$Conc_{i0}$ (M)	$Conc_{i0}$ (g/g) × 10^{-3}	Average Area (× 10^{-9})
0.03	2.71	0.25
0.05	4.52	0.40
0.10	9.04	0.83
0.15	13.56	1.26
0.20	18.08	1.55
0.30	27.12	2.33
0.40	36.16	3.15
0.50	45.20	3.82
0.55	49.72	4.20

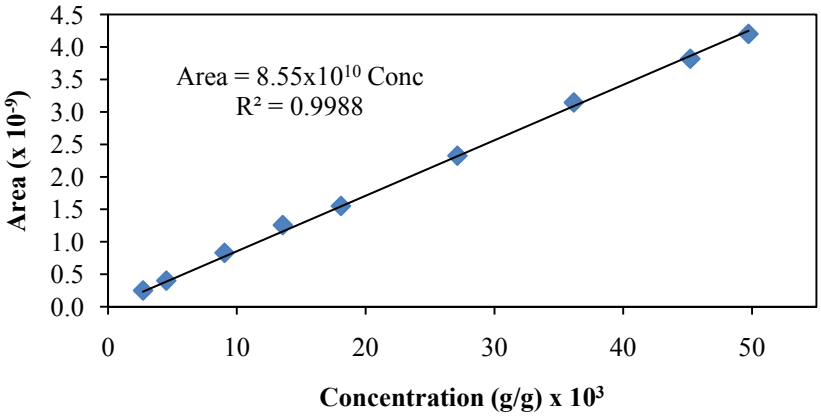

Figure B1. Calibration curve for L-lactic acid.

B2. Calibration curve for L-malic acid

In order to determine the amount of L-malic acid in each phase, a calibration curve was used. For this purpose, seven standards of different known concentrations of L-malic acid were prepared in water. Table B2 presents the concentration of the prepared standards in M and in g of solute/g of solution and the respective average area of the picks acquired. Figure B2 presents the calibration curve obtained and respective slope and correlation coefficient.

Table B2. L-malic acid standards and respective area.

$Conc_{i0}$ (M)	$Conc_{i0}$ (g/g) × 10^{-3}	Average Area (× 10^{-9})
0.03	3.43	0.37
0.05	6.85	0.76
0.08	10.28	1.08
0.10	13.70	1.48
0.20	27.41	2.75
0.40	54.81	5.23
0.50	68.51	6.57

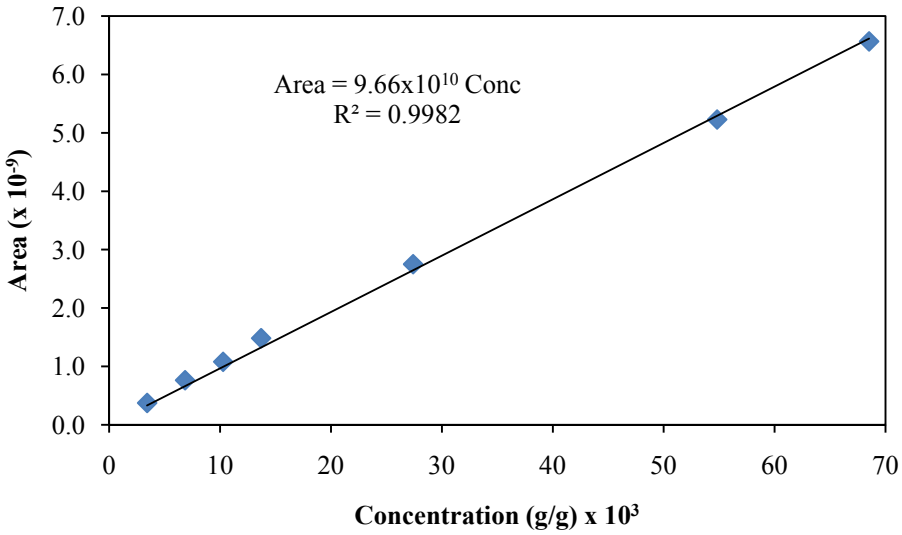

Figure B2. Calibration curve for L-malic acid.

B3. Calibration curve for succinic acid

In order to determine the amount of succinic acid in each phase, a calibration curve was used. For this purpose, nine standards of different known concentrations of succinic acid were prepared in water. Table B3 presents the concentration of the prepared standards in M and in g of solute/g of solution and the respective average area of the picks acquired. Figure B3 presents the calibration curve obtained and respective slope and correlation coefficient.

Table B3. Succinic acid standards and respective area.

$Conc_{i0}$ (M)	$Conc_{i0}$ (g/g) × 10^3	Average Area (× 10^{-9})
0.02	2.37	0.17
0.04	4.74	0.36
0.06	7.11	0.49
0.08	9.48	0.64
0.10	11.85	0.79
0.15	17.77	1.20
0.20	23.69	1.57
0.30	35.53	2.38
0.50	59.22	3.97

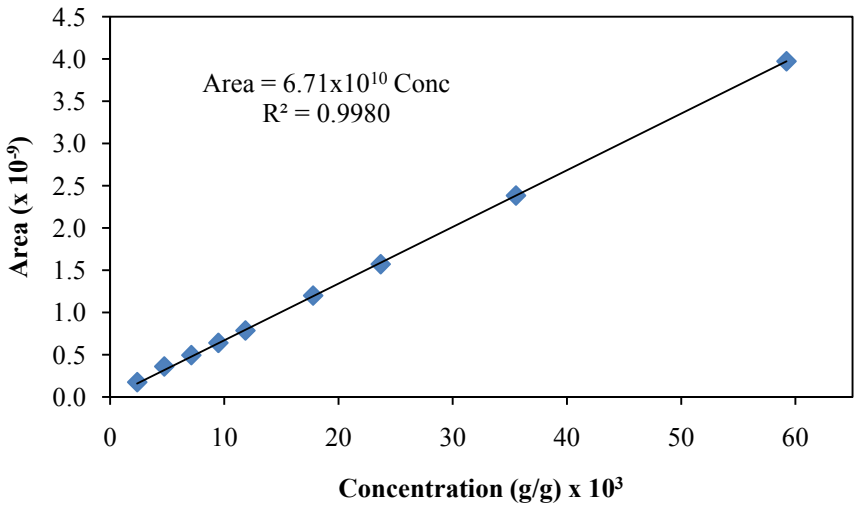

Figure B3. Calibration curve for succinic acid.