Extraction of short-chain organic acids using imidazolium-based ionic liquids from aqueous media

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ABSTRACT

The biological routes have been a competitive alternative for organic compounds especially the organic acids. However, the main factor restrained the application of biological routes in large scale is the cost of organic acids separation. Ionic liquids have been claimed to have the potential to achieve the separation of organic acids. In this paper, the interphase distribution of three organic acids in systems involving five different imidazolium-based ionic liquids had been analyzed. Results showed that hydrophobicity and concentration of organic acid, alkyl chain on the cation and anion of the ionic liquids, the pH of the extraction system all could affect the extraction efficiency. Additionally, the back extraction of organic acids from ionic liquids into distilled water could be up to 81%. The results indicated ionic liquids are potentially useful in the recovery of organic acids from diluted broths, and they also provided useful information for designing special ionic liquids for extraction.

Key words: Ionic liquid; Organic acid; Extraction efficiency; Partition coefficient; Recovery

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INTRODUCTION

Organic chemicals are normally derived from fossil feedstock via chemical routes. However, the shortage of fossil resources and the demand for sustainable development increase the cost of organic chemicals [1]. As the development of bio-technology, the biological routes for organic chemicals have been a competitive alternative [2]. Among the numerous organic chemicals, organic acids constitute an important part. Since last century, many organic acids (such as lactic acid (LA), citric acid, succinic acid, and glutamic acid) have been produced using renewable biomass as the main feedstock [3, 4]. As reported, the estimate market size of succinic acid is up to 270,000 tons annually [5]. And the citric acid is over 1.4 million tons per year [6].

Although many organic acids have been produced using renewable biomass as the main feedstock since last century, the main factor restrained the use of biological routes in large scale is the separation cost of desired acids from the diluted fermentation broth, which constitutes 60%-80% of the overall cost [7, 8]. The traditional recovery methods of organic acids include precipitation, ion-exchange resin, solvent extraction, membrane separation [8-10], etc. However, precipitation will bring valueless by-products. The organic solvents used in solvent extraction cause some associated problems such as toxicity, volatility. Besides, the price of these volatile organic compounds (VOCs) and their safe engineering increase the cost of separation. The membrane fouling and high cost of membrane limit the widespread use of membrane separation [11]. Therefore, more effective extraction processes are desired to be established for the development of biological routes of organic chemicals.

In recent decades, ionic liquids (ILs), a group of organic salts, have attracted more and more attentions. Most of ILs is composed of an organic cation and either an organic or inorganic anion. Compared to many other organic solvents,

ILs possesses a practically zero vapor pressure, higher density, low solubility in water, and environmentally benign feature. Therefore, they are treated as potential "green solvents"[12]. Besides, the unique ionic character of ILs and their "structure and organization" can lead to specific effects and make them different from molecular solvents. Nowadays, there is an increasing interest in the application of ILs for separating organic compounds from fermentation broth[13]. Chen et al. adopted imidazolium-based ILs instead of toxic organic solvents to extract caprolacctam from aqueous solutions and higher distribution ratios for caprolactam into ILs were obtained than into benzene or toluene[14].Solvent extraction of lactic acid by phosphonium ILs (CyphosIL-104) was studied by Schlosser et al. and the results showed that H-bond coordination could explain the increased distribution coefficient of lactic acid by CyphosIL-104[15].Khachatryanet al. studied the extraction of phenols from aqueous solution by 1-butyl-3-methylimidazolium hexafluorophosphate at pH <pKa and nearly quantitative extraction of phenols were observed. However, the recovery of phenols from ILs was not ideal[16]. Wang et al. investigated the recovery of several amino acids from fermentation broth by imidazolium-based ILs and they found the extraction efficiency could be greatly influenced by the pH, the alkyl chain length on the cation, and the anion nature of the ILs[17].Oliveira et al. applied hydrophobic ILs for extraction of L-lactic, L-malic, and succinic acid from aqueous solutions with partition coefficients from 1.1 to 20.9[18].Though many progress have been made on the extraction of organic chemicals with ILs, all the recovery process were either not considered back extraction of organic acids from ionic liquids or with a poor result.

Imidazolium-based ILs is one group of the most common ILs, which is nonvolatile, inexpensive, chemical stable and easy to operate. Besides, liquid state and hydrophobic character are also outstanding features[19].In the present study, a series ofimidazolium-based ILs(see Table 1) were applied in the recovery of three short chain organic acids (see Table 2) from aqueous solutions. Three different anions of ILs, with different anions and alkyl chain length on the cations, were selected to research the factors that affect the extraction degree of organic acids from aqueous solution (see Table 1). The organic acids listed in the Table 2 with different chemical structures were chosen due to the difference of their hydrophobicity. In addition, they all have great potential in chemical raw materials. The objectives of this work were to find the rules for extraction of organic acids from fermentation broth by imidazolium-based ILs and explore green extraction methods for the green biological synthetic method of organic acids.

EXPERIMENTAL SECTION

MATERIALS
Aqueous lactic acid (LA, CAS 79-33-4, 98%), and solid citric acid (CA, CAS 77-92-9) were supplied by Sinopharm Chemical Reagent Co., Ltd. Mevalonic acid were biosynthesized using engineered *Escherichia coli* with basic purification (Table 1). Deionized water was used for preparation of acid solutions. Sodium hydroxide and hydrochloric were applied to adjust the pH of aqueous solutions.

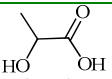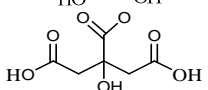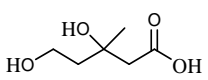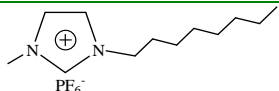**Table 1List of organic acids used, and their properties at 298.15 K**
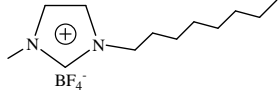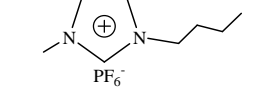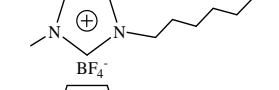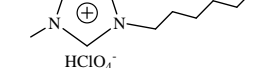
Compounds	CAS	pKa	Structure	Solubility (g/L)
Lactic acid	50-21-5	3.91		776
Citric acid	77-92-9	2.93		999
Mevalonic acid	150-97-0	4.33		366

Table 2Structure of the ILs and other details

Compound	Formula	CAS	Structure
1-octyl-3-methylimidazolium hexafluorophosphate ([C$_8$mim][PF$_6$])	C$_{12}$H$_{23}$PF$_6$N$_2$	304680-36-2	
1-octyl-3-methylimidazolium tetrafluoroborate ([C$_8$mim][BF$_4$])	C$_{12}$H$_{23}$BF$_4$N$_2$	244193-52-0	
1-butyl-3-methylimidazolium hexafluorophosphate ([C$_4$mim][PF$_6$])	C$_8$H$_{15}$PF$_6$N$_2$	174501-64-5	
1-hexyl-3-methylimidazolium tetrafluoroborate ([C$_6$mim][BF$_4$])	C$_{10}$H$_{18}$BF$_4$N$_2$	244193-50-8	
1-hexyl-3-methyl imidazole perchlorate ([C$_6$mim][HClO$_4$])	C$_{10}$H$_{19}$ClN$_2$O$_4$	648424-43-5	

1-octyl-3-methylimidazolium hexafluorophosphate ([C$_8$mim][PF$_6$], CAS 304680-36-2), 1-octyl-3-methylimidazolium tetrafluoroborate ([C$_8$mim][BF$_4$], CAS 244193-52-0), 1-butyl-3-methylimidazolium hexafluorophosphate ([C$_4$mim][PF$_6$], CAS 174501-64-5), 1-hexyl-3-methylimidazolium tetrafluoroborate ([C$_6$mim][BF$_4$], CAS 244193-50-8), and 1-hexyl-3-methyl imidazole perchlorate ([C$_6$mim][HClO$_4$], CAS 648424-43-5) were provided by Shanghai ChengJie Chemical Co. LTD. The purity of all ILs was more than 99%, and no further purification was carried out.

EXPERIMENTAL PROCEDURES
Aqueous solutions, containing $(5-80.0) \times 10^{-3}$ mol L^{-1} of organic acids, were prepared for the extraction studies at room temperature (20 ± 1 ℃). All the solutions presented pH values were adjusted with hydrochloric acid and sodium hydroxide solution. A pH meter with a combination pH electrode was used to measure the pH of the aqueous phase. A known amount of different organic acids were dissolved in distilled water. 1.0 ml of pure IL was contacted with the same volume of organic acids' solution. 50 ml test tubes were used to conduct the experiment and the system was vigorously stirred to attain equilibrium. Then, the mixture was centrifuged to ensure clean separation for the phases. Two-step extraction was also performed in the same ratio (v/v=1) as the single-step extraction and carried out at the same conditions[17].

DETECTION METHODS
The acid present in both phases were quantified using a Water 1525 HPLC, with an UV light detector at a wavelength of 211 nm. HPLC system is consisted of HPx-87H (250×3 mm) separation column and pump. The mobile phase was 0.1 mmol L^{-1}H$_2$SO$_4$in column, the column temperature was kept as 308 k and the flow was constant at 0.1 mlmin^{-1}. External standard was used to build the calibration, by analyzing the samples with known amount. Three calibration curves were established for the three different acids. The concentration of each acid in both aqueous and IL phases was calculated using these calibration curves.

CALCULATION MEHODS
When the IL and aqueous solution was at the same volume, the partition coefficients of organic acids between the IL and aqueous solution (K$_{IL/W}$)were defined by Eq. (1). The efficiency of the extraction of different ILs (EE%) were determined according to Eq. (2).

$$K_{IL/W}= (C_i-C_f)/C_f \tag{1}$$

$$EE(\%)=(C_i-C_f)/C_i \tag{2}$$

Where C$_i$refers to the initial concentration of organic acid quantified in aqueous liquid, in g of acid/ml of solution, and C$_f$is the finial concentration of organic acid in aqueous phase.

RESULTS AND DISCUSSION

EFFECT OF CHEMICAL STRUTURE OF ILs
The chemical structures of the ILs have been proved to be important on the effect of partition coefficients and the

extraction efficiencies of organic acids.Table 3-5revealed the data forall five ILs at four different concentrations of organic acids. As can be seen from Table 3-5, partition coefficients of organic acids into $[C_6mim][BF_4]$ are higher than others under the same conditions. For example, the $K_{IL/W}$value of lactic acid into $[C_6mim][BF_4]$ is nearly 30 times than that into $[C_8mim][PF_6]$ at pH=0.9 and C_i=1.2 M.

Anions predominate in the partition coefficients of the organic acids from broth. Partition coefficients of the organic acids into $[C_8mim][BF_4]$ are much higher than those into $[C_8mim][PF_6]$ under the same conditions. For example, the partition coefficient of lactic acid into $[C_8mim][BF_4]$ is almost 3 times higher than that into $[C_8mim][PF_6]$ at 0.2 M. The similar phenomenon can also be drawn between $[C_6mim][BF_4]$ and $[C_6mim][HClO_4]$. As reported,the effective negative charge in PF_6^-or $HClO_4^-$anion is much weaker than that in BF_4^-anion. Therefore, electrostatic interactions between the cationic form of the organic acids and the BF_4^- anion should be stronger. A higher extraction degree is expected by BF_4^-based ILs[14, 17].

Table 3 Effect of the concentration of citric acid on the partition coefficient($K_{IL/W}$) at 293.15 K

IL	Concentration (M)	C_i	C_{IL}	C_f	$K_{IL/W}$	EE(%)
	0.05	9.5	0.05	9.45	0.01	0.5
$[C_8mim][PF_6]$	0.1	20.8	0.1	20.7	0.01	0.5
	0.2	38.4	17.0	21.4	0.80	44.3
	1.2	219.7	12.4	207.3	0.06	5.6
	0.05	9.5	1.6	7.9	0.21	16.9
$[C_8mim][BF_4]$	0.1	20.8	3.6	17.2	0.21	17.3
	0.2	38.4	16.8	21.6	0.78	43.9
	1.2	219.7	57.5	162.2	0.36	26.2
	0.05	9.5	0.1	9.4	0.01	1.1
$[C_4mim][PF_6]$	0.1	20.8	0.8	20	0.04	3.9
	0.2	38.4	3.72	34.7	0.11	9.7
	1.2	219.7	15.6	191.1	0.08	7.1
	0.05	9.5	2.0	7.5	0.27	21.2
$[C_6mim][BF_4]$	0.1	20.8	5.1	15.7	0.33	24.5
	0.2	38.4	13.6	24.8	0.55	35.4
	1.2	219.7	69.3	150.4	0.46	31.6
	0.05	9.5	0.8	8.7	0.09	8.4
$[C_6mim][HClO_4]$	0.1	20.8	1.9	18.9	0.10	9.1
	0.2	38.4	16.5	21.9	0.75	43.0
	1.2	219.7	39.8	180.0	0.22	18.2

Table 4 Effect of the concentration of lactic acid on the partition coefficient($K_{IL/W}$) at 293.15 K

IL	Concentration (M)	C_i	C_{IL}	C_f	$K_{IL/W}$	EE(%)
	0.05	3.5	0.1	3.4	0.03	3.4
$[C_8mim][PF_6]$	0.1	8.3	0.17	8.13	0.02	2.1
	0.2	22	9.2	12.8	0.72	42.0
	1.2	102.5	17.6	84.9	0.21	17.3
	0.05	3.5	1.0	2.5	0.40	28.6
$[C_8mim][BF_4]$	0.1	8.3	2.3	6.0	0.38	27.7
	0.2	22	15.3	6.7	2.31	69.8
	1.2	102.5	44.4	58.1	0.92	43.3
	0.05	3.5	0.2	3.3	0.06	5.7
$[C_4mim][PF_6]$	0.1	8.3	0.26	8.04	0.03	3.2
	0.2	22	15.0	7.0	2.14	68.2
	1.2	102.5	19.7	82.8	0.24	19.3
	0.05	3.5	1.1	2.4	0.46	31.4
$[C_6mim][BF_4]$	0.1	8.3	2.5	5.8	0.43	30.3
	0.2	22	10.9	11.1	1.02	49.6
	1.2	102.5	51.8	50.7	1.11	55.4
	0.05	3.5	0.8	2.7	0.30	22.9
$[C_6mim][HClO_4]$	0.1	8.3	1.9	6.3	0.30	23.3
	0.2	22	9.9	12.1	0.82	45.0
	1.2	102.5	41.2	61.3	0.67	40.4

From the analysis of Table 3-5, it is interesting to point that the phase preference for the organic acids decreased as the length of alkyl chain on the cation decreased from C_8 to C_4.It was similar to the studies by Chenet al., they observed the order of extractability for caprolactam by ILs as follows: $[C_8mim][PF_6]$ < $[C_6mim][PF_6]$ < $[C_4mim][PF_6]$ < $[C_6mim][BF_4]$[14]. In this studies, the partition coefficient of mevalonic acid is 1.0 into $[C_8mim][BF_4]$ and 1.21 into $[C_6mim][BF_4]$ in pH=0.9and C_i=0.2 M, respectively. Similar results were observed in $[C_4mim][PF_6]$ and $[C_8mim][PF_6]$at the same conditions, which was also found in the extraction of amino acids with imidazolium-ILs. One sound explanation is that the fluorine of the anion in $[C_4mim][PF_6]$, $[C_6mim][BF_4]$, and

$[C_8mim][BF_4]$ can form a stronger hydrogen bond associations with the H2 of the imidazolium ring[20, 21]. As the alkyl chain on the imidazolium ring gets longer, the screening effect or steric hindrance effect for the electrostatic attractive interactions of the cationic form of organic acids with the anion of the ILs may be stronger[17].Kumaret al. also found the aggregation behavior of ILs, which may be affected by alkyl chain length and different anions. And this aggregation behavior may have an important role in the extraction of organic acids from aqueous solution [22].

Table 5 Effect of the concentration of mevalonic acid on the partition coefficient($K_{IL/W}$) at 293.15 K

IL	Concentration (M)	C_i	C_{IL}	C_f	$K_{IL/W}$	EE(%)
	0.05	6.6	1.1	5.5	0.20	16.8
	0.1	19.2	5.9	13.3	0.45	30.7
$[C_8mim][PF_6]$	0.2	31.4	5.6	25.8	0.20	17.8
	1.2	189.1	92.7	96.4	0.96	49.1
	0.05	6.6	2.47	4.13	0.60	37.4
	0.1	19.2	8.0	11.2	0.71	41.6
$[C_8mim][BF_4]$	0.2	31.4	17.0	17.1	1.01	54.1
	1.2	189.1	123.2	65.9	1.87	65.2
	0.05	6.6	1.68	4.92	0.34	25.5
$[C_4mim][PF_6]$	0.1	19.2	6.5	12.7	0.55	33.9
	0.2	31.4	8.1	26.0	0.31	25.8
	1.2	189.1	102.4	86.7	1.20	54.2
	0.05	6.6	2.99	3.61	0.83	45.3
$[C_6mim][BF_4]$	0.1	19.2	8.2	11.0	0.76	42.7
	0.2	31.4	18.0	13.4	1.34	57.3
	1.2	189.1	127.8	61.3	2.09	67.6
	0.05	6.6	3.23	3.4	0.96	48.9
$[C_6mim][HClO_4]$	0.1	19.2	8.0	11.2	0.64	40.2
	0.2	31.4	13.0	21.1	0.62	42.0
	1.2	189.1	130.1	59.0	2.21	68.7

These extremely astonishing differences reflected that IL anions and the alkyl chain length on the cation of ILs played an important part in partition coefficients andextraction efficiencies.

EFFECT OF HYDROPHOBICITY OF ORGANIC ACIDS

Chemical structure of organic acids in Table 2 reveals that mevalonic acid has an additional –OH group, an additional –CH_3 group, an additional –C group and two additional –CH_2 group compared with lactic acid, while citric acid has one –OH group and three –COOH group. The solubility of mevalonic acid in water at 25℃ is 366 g L^{-1}, while the lactic acid and citric acid are 776 g L^{-1} and 999 g L^{-1}, respectively. The solubility shows some features for the hydrophobicity of these three organic acids in water at a given condition: mevalonic acid > lactic acid > citric acid.

Some interesting features for the partition coefficients of the organic acids into a particular ILs were revealed according to the data in Tables 3-5 at pH=0.9. It seems that the extractability of the organic acid by ILs increase in the order: citric acid < lactic acid <mevalonic acid. For instance, the partition coefficient value of mevalonic acid is 2.09 when it was extracted by $[C_6mim][BF_4]$ at 1.2 M, while the lactic acid was 1.11 and citric acid was 0.46. The partition coefficient values of mevalonic acid, lactic acid, citric acid were 0.69, 0.38, 0.21, respectively, when they were extracted by $[C_8mim][BF_4]$ at 0.1 M. Mevalonic acid is at the form of mevalonlactone at pH=0.9, which is more hydrophobicity. These trends suggested the higher hydrophobicity of organic acid is, the lower affinity of organic acid will be to the aqueous phase than the ionic liquid phase.

EFFECT OF pH ON THE PARTITION COEFFICIENTS

The effect of the pH on the partition coefficients of organic acids were shown in Fig.1. It is clearly shown that, in the range of pH <pKa, $K_{IL/W}$ values of the organic acids decrease sharply as the increase of pH. Similar results can be found in others' investigations. As reported, the pH of aqueous solutions has a great effect on the charged characteristics of organic acids.The hydrophilic groups of organic acids can be ionized, leading to different equilibrium forms at different pH of the aqueous phase: cationic form, zwitterionic form, and anionic form. Belovaet al. analyzed the solvent extraction of weak organic acids in binary extractants and concluded that acidic solutions were most effective for the extraction of acids[23]. Wang and Pletnevet al. also came to the similar conclusion[16, 17].In the range of pH <pKa, the cationic form is predominant in aqueous phase and the percentage of the cationic form decreases with the increasing pH of the aqueous phase[17]. It seems that the decreased partition coefficients are related to the decreased percentage of the cationic form of organic acids. The effect of the pH on the partition coefficients of mevalonic acids are more efficiently than other acids (Fig. 1). It is because mevalonic acid can form mevalonlactone at low pH, which has a lower affinity to the aqueous phase. According to this phenomenon, it is suggested that the extraction process has an important relationship with the electrostatic interactions between the

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cationic form of the organic acids and the anion of the ILs. And the stronger electrostatic interaction is, the higher partition coefficient of the organic acids will be.
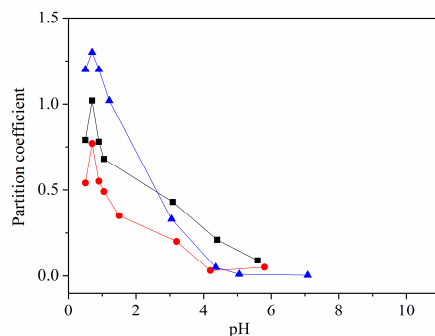

Fig.1: Effect of pH on the partition coefficients ($K_{IL/W}$) at 293.15 K with [C_6mim][BF_4]. (●) citric acid, (■) lactic acid, (▲) mevalonic acid

EFFECT OF CONCENTRATION

For the studied acids, it is clear that both the partition coefficient and extraction efficiency of citric acid increased with the increase of acid concentration, while the partition coefficient and extraction efficiency of lactic acid and mevalonic acid increased in the range of 0.05 M to 0.2 M and decreased between 0.2 M and 1.2 M.

The concentration seems to have some effects on the hydrophobicity of organic acids. Almost three times of partition coefficient may be enhanced by the changes in the concentration of organic acids. For example, when mevalonic acid was extracted by [C_8mim][BF_4] from 0.1 M, 0.2 M, 1.2 M fermentation broth, the partition coefficient of mevalonic acid were 0.69, 1.0, 1.84, respectively. The low concentration of organic acid make it ionized to cationic form more easily, which is harder to be extracted from aqueous phase to ionic liquid phase[18].In the case of mevalonic acid, the partition coefficients are increased between 0.2 M and 1.2 M, which was different from citric acid and lactic acid. The IL is one of the special surfactants and performs associating electrolyte behavior at high concentration[24]. And the hydrophobicity of mevalonic acid is stronger than two other organic acids. The interaction between water and mevalonic acid may decrease with the increase of acid concentration when the concentration of IL is high. This may explain why the partition coefficient increased with the increase of acid concentration whenmevalonic acid was extracted.

TWO-STEP EXTRACTION

The partition coefficients of single-step extraction were almost less than 1 and the extraction efficiencies were almost less than 50%. For the three studied organic acids, about 50% of the acid was remained in the aqueous solution. To improve the partition coefficients and extraction efficiencies of acids from aqueous solutions, two-step extraction was conducted at 293.15 K for all the three acids at 0.2 M and 1.2 M. The [C_6mim][BF_4] was chosen as extractant due to its higher efficiency.
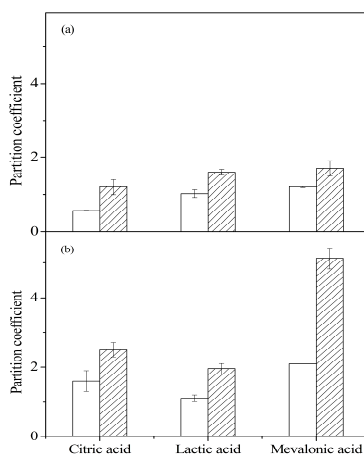

Fig. 2 Partition coefficients, $K_{IL/W}$, for the one step ( ) and two step (▨) extractions of the studied organic acids, at 293.15 k with [C_6mim][BF_4].(a) For concentration of 0.2 M, (b) For concentration of 1.2 M

Fig.2showed the partition coefficients of two-step extraction at 0.2 M and 1.2 M. From the analysis of data, it is obvious that the partition coefficients of two-step extraction were much higher than that of the single-step extraction. For the citric acid, the partition coefficient of the two-step extraction increased nearly three times. In the case of lactic acid and mevalonic acid, both of the partition coefficients could reach to 1.7 at 0.2 M. The partition coefficient of the mevalonic acid can reach to 5.13 and the extraction efficiency was 83.3% after the second extraction at 1.2 M. Compared to 0.2 M, it suggested that the concentration of organic acids do have an important role on the behave of IL.

RECOVERY PROCEDURE

The previous studies showed that ILs have the ability to extract the organic acids from aqueous solutions efficiently. Nevertheless, it is necessary to recover the acids from the IL phase. Low-pressure distillation and pH variation had once been used by Oliveira et al.for the stripping of organic acids from IL phase, but these two methods were not efficient enough. The amount of distillate was even too small to be quantified by low-pressure distillation, and only a small amount of acid could be recovery from ILs[15, 18].The recovery of phenolic compounds from Imidazolium-based ILs was also researched by Khachatryanet al. and it was incomplete. Matsumoto et al. investigated the separation of several short-chain organic acids (acetic, lactic, pyruvic, butyric acid) from water using 1-alkyl-3-methylimidazoliumhexafluorophosphates. The extraction behaviors of ILs were not quite well and no recovery process was conducted[25].
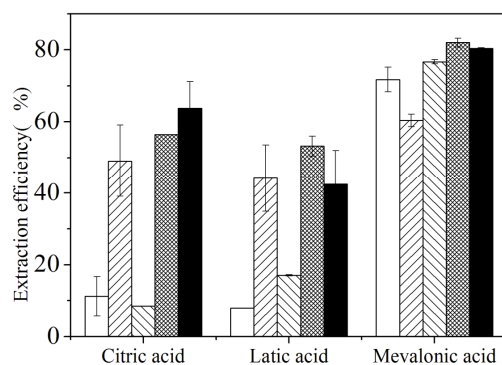

Fig.3 The extraction efficiency of back extraction for concentration of 0.2 M at the given pH (pH = 0.9), 293.15 k. For the extraction with [C$_8$mim][PF$_6$] (   ), [C$_8$mim][BF$_4$] (   ), [C$_4$mim][PF$_6$] (   ), [C$_6$mim][BF$_4$] (   ), [C$_6$mim][HClO$_4$] (   ).

In this study, the back extraction of organic acids from ILs was investigated at room temperature. The original concentration of organic acids was 0.2 M at pH= 0.9. As shown in Fig. 3, the mevalonic acid was more easily back extracted into distilled water and the extraction efficiency could be up to 81%. The citric acid and lactic acid had a lower partition coefficients of back extraction, but they were also could reach to 56%. The difficulty of back extraction was citric acid > lactic acid >mevalonic acid. It seems likely that there is a correlation between the partition coefficients of back extraction and the pH of distilled water. As demonstrated above, the ionic form is predominant in aqueous phase and the mevalonic acid is not in the form of mevalonlactone in the range of pH >pKa, thus making organic acids have higher affinity to the aqueous phase and be back extracted from ILs more easily.

From the ILs investigated in this work, it is also interesting to find that the partition coefficient of back extraction followed the trend: [C$_6$mim][BF$_4$] > [C$_6$mim][HClO$_4$] > [C$_4$mim][PF$_6$] > [C$_8$mim][BF$_4$] > [C$_8$mim][PF$_6$]. This back extraction trend is similar to the extraction of organic acids from aqueous solution to ILs, and the most effective ILs of back extraction was also [C$_6$mim][BF$_4$]. It is evident from the above results that the stronger effective negative charge in the anion will be more efficient for the extraction, such as BF$_4^-$, which can be combined with the shorter alkyl chain on the imidazolium ring to reach a higher extraction efficiency and back extraction efficiency of organic acids from fermentation broth. In this way, it provides data for the design of ILs for the extraction of organic acids.

CONCLUSION

The stability of ILs in a wide temperature range and their negligible vapor pressure are two outstanding properties distinguished from conventional organic solvents. In this study, we examined weather imidazolium-based ILs could be used as extractants instead of organic solvents for the extractive separation of organic acids from aqueous media and they exhibited good performance. The hydrophobicity effect and concentration of the organic acids seems to be

driving forces for the extraction of organic acids from aqueous solution into ILs. The ILs with a stronger negative charge and shorter alkyl chain on the imidazolium ring are more effective in the range of pH <pKa. The extraction efficiency of [C$_6$mim][BF$_4$]for mevalonic acid can be up to 67.6%, and the extraction efficiency of two-step was 83.3%. Anther outstanding point of this research was the recovery of organic acids from ILs. Compared to other researches, the mevalonic acid was easily back extracted into distilled water and the extraction efficiency could be up to 81%.The researches herein illustrated the potential separation of organic acids from fermentation broth using imidazolium-based ILs, which showed excellent performance. The structure of ILs can be designed based on these results for better extraction. Further studies will focus on the design of ILs with high selectivity for specific organic acid in order to meet the need of industrial extraction of organic acids.

Acknowledgements

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