



Recovery of methacrylic acid from dilute aqueous solutions by ionic liquids through hydrogen bonding interaction



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ABSTRACT

The recovery of carboxylic acids from dilute aqueous solution is necessary but difficult in chemical industry. Methacrylic acid (MAA) is an important chemical widely used in polymer industry. In this work, the recovery of carboxylic acid from diluted aqueous solution by liquid–liquid extraction using ionic liquids (ILs) as extractants was studied. MAA was employed as model carboxylic acid. The partition coefficients of MAA in biphasic system and the extraction efficiencies of MAA were determined for imidazolium-based ILs and quaternary ammonium salt ILs with different structure of cation and anion. The extraction conditions such as extraction time, extraction temperature, mass ratio of ILs to MAA aqueous solution, initial concentrations of MAA, and water content were evaluated. An internal mechanism of the MAA extract by ILs was revealed by combining solvatochromic study, FT-IR and quantum chemical calculations. The results show that the strong hydrogen bond basicity (β) of ILs results in the high partition coefficient of MAA, which provides guidance to molecular design of ILs for the high efficient extractive separation of MAA from diluted aqueous solution. Based on this, IL with strong hydrogen bond basicity ($[N_{8881}]Cl$) was used to extract MAA from dilute aqueous solution. Compared with hexane which is conventional solvent used in MAA extractive separation, $[N_{8881}]Cl$ can get 49 times higher of partition coefficient value and the extraction efficiency reach 94.57% for the single-stage extraction.

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1. Introduction

Carboxylic acids are important raw material for food, chemical and pharmaceutical industries [1]. Due to the strong affinity of carboxylic acids to water, the isolation and purification of carboxylic acids from aqueous solution is rather difficult, especially for the recovery of carboxylic acids from dilute aqueous solution (< 10 wt%), such as recovery of propanoic acid, acrylic acid and methacrylic acid from downstream and waste water of the acid produce process. It is a high energy consumption process and easy cause secondary pollution. Thus the recovery of carboxylic acids from dilute aqueous solution remains interest to researchers [2–5].

There are several kinds of techniques that can be used for carboxylic acids recovery from dilute aqueous solution, such as direct distillation, solvent extraction, adsorption [4], anion exchange [6], electrodialysis [7], and reverse osmosis. Since carboxylic acids are easy formed hydrogen-bonded dimers rather than individual molecules, the boiling point of carboxylic acids always higher than

water (the boiling point of the simplest carboxylic acid, formic acid, is 374.15 K). It is high energy consumption process for vaporization of a large amount of water. Thus direct distillation is not suitable for separate acid from dilute aqueous solutions. Adsorption and ion exchange are high efficient techniques for the recovery of carboxylic acids from very dilute aqueous solutions. However, these processes require large amount of chemicals to regenerate absorbent or ion-exchange resin [8]. The membrane separation techniques of electrodialysis and reverse osmosis have advantage of separation and concentration of carboxylic acids from very dilute aqueous solutions. Yet, membrane is susceptible to contamination and decreases separation performance. Compared with these methods (except distillation), solvent extraction is kind of well-established, easy to reliably scale up technology and commonly used to separate carboxylic acids from aqueous solutions [9–12]. There are various solvents commonly used for the extraction of carboxylic acids, such as toluene, xylene and heptane [13]. However, the low aqueous activity of carboxylic acids results in low partition coefficients of carboxylic acids into these conventional solvents, especially for the recovery of carboxylic acids from dilute aqueous solution. Thus, solvent extraction with

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conventional solvents require very high solvent flow rates, which results in substantial dilution of the acids and increase the cost of extractant recovery. Meanwhile, the use of organic solvents brings up some associated problems such as volatility and flammability, which implies additional environmental hazards effects. Nowadays, green chemistry and engineering has become common understanding in both academia and industry. Hence it is urgent to search a green and highly efficient extractant to extract carboxylic acids from dilute aqueous media.

Ionic liquids (ILs) have some good properties such as very low vapor pressure, non-flammable and wide range of liquids. Meanwhile, ILs has strong solvation ability for both inorganic and organic substance because of the specific ILs structure [14]. There are growing interests using ILs as extractants to separate some organic compounds, such as carboxylic acids [15–17], alcohols [18,19], phenolic compounds [20,21]. ILs has shown better separation efficiency in extraction process as compared with the conventional organic solvents [22,23]. A possible reason is the strong hydrogen bonding, π - π , van der Waals and electrostatic interaction between ILs and solutes. For example, solutes with hydrogen bond donor group, such as indole [24], tocopherols [25], can be recovered by liquid-liquid extraction using appropriate ILs due to the strong hydrogen bonding interaction between ILs and these solutes. Moreover, the interaction between ILs and solute molecules can be adjusted by tuning the structure of the cations and anions of ILs for separation of the goal solute from mixtures by ILs [26]. This makes ILs become potential extractants for separate carboxylic acids from its aqueous solution.

Methacrylic acid (MAA) is an important monomer in polymer manufacturing and has widely used in modern industry and engineering [27], pharmaceutical industry [28], and chromatographic analysis [29], etc. Typically, MAA is produced by the oxidation of isobutane or methacrolein [30,31]. In this process, MAA is absorbed by water and produced as a diluted aqueous solution. Thus, MAA was used as model carboxylic acids in this work. The imidazolium-based ILs and quaternary ammonium salt ILs were used to separate MAA from the aqueous solution. A series of ILs with different structures were investigated through the extraction efficiency and partition coefficient of MAA. Moreover, the effects of the structure of ILs and extraction conditions, such as extraction time, initial concentration of MAA, extraction temperature, mass ratio, and water content were studied. The mechanism of the extraction process was explored by experimental method (FT-IR, solvatochromic study). Furthermore, the interaction of MAA with ILs was analyzed by quantum chemical calculations. Meanwhile, the solvation effect of MAA in IL was also considered. Based on the analysis of the extraction mechanism of ILs, the IL with better performance to extract MAA from dilute aqueous solution was selected. The recycling performance of the IL was also studied.

2. Material and methods

2.1. Materials

1-methylimidazole (99%), 1-bromohexane (99%), 1-chlorooctane (99%), potassium hexafluorophosphate (99%), sodium fluoroborate (99%), and methyltrioctylammonium chloride ($[N_{8881}]Cl$) were purchased from Aladdin Industrial Corporation (China). 1-chlorobutane (99%) and methacrylic acid (99%) were purchased from Alfa Aesar (China). Lithium bis(trifluoromethanesulfonyl)imide (99%) was purchased from J&K Scientific (China). These chemicals were commercially available and used as received. Ethyl acetate (99.5%), acetonitrile (99%), dichloromethane (99.5%) and methanol (99.9%) were purchased from Xilong Chemical Co., Ltd (China). Acetone (99.5%) was purchased from Beijing Chemical Works (China). These

chemicals were dried before using to make sure the water contains below 500 ppm.

2.2. Preparation of ILs

The ILs were synthesized according to previous literature [32]. Typically, the precursor 1-butyl-3-methylimidazolium chloride ($[bmim]Cl$) was prepared by alkylation of 1-methylimidazole with 1-chlorobutane. Then the goal IL 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ($[bmim]Tf_2N$) was prepared by metathetic reaction of $[bmim]Cl$ with Lithium bis(trifluoromethanesulfonyl)imide ($Li(Tf_2N)$). After the reaction, IL was dissolved in dichloromethane and washed by deionized water to remove soluble inorganic salt. Then the volatile material in the IL was removed under reduced pressure (0.1 bar, 0.1 mm) at 353.15 K for 2 h to afford $[bmim]Tf_2N$. The same procedure was applied for the preparation of 1-hexyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ($[hmim]Tf_2N$), 1-octyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ($[omim]Tf_2N$), 1-butyl-3-methylimidazolium hexafluorophosphate ($[bmim]PF_6$), 1-hexyl-3-methylimidazolium hexafluorophosphate ($[hmim]PF_6$), 1-octyl-3-methylimidazolium hexafluorophosphate ($[omim]PF_6$), 1-hexyl-3-methylimidazolium tetrafluoroborate ($[hmim]BF_4$), 1-octyl-3-methylimidazolium tetrafluoroborate ($[omim]BF_4$), methyltrioctylammonium bis(trifluoromethanesulfonyl)imide ($[N_{8881}]Tf_2N$) ILs.

The prepared ILs was characterized by their 1H NMR (600 MHz, DMSO- d_6) and FT-IR spectra. The details can be found in [Supplementary Material](#). The water content was measured by Karl-Fischer titration method. The chloride content was determined by turbidimetry method. The water content and chloride content, along with experimental densities and viscosities of the ILs used in this work are shown in [Table 1](#).

2.3. Extraction procedures

The extraction experiments were performed as follows: a known amount of MAA aqueous solution and IL was added to a glass vessel which was equipped with magnetic stirrer and water bath. The mixture was vigorously stirred for 2 h at a certain temperature, and then allowed to settle for at least 4 h at the same temperature. Samples were taken from each of the two phases and diluted with methanol for UPLC analysis.

2.4. UPLC analysis

The UPLC systems consisted of an auto sampler, an Acquity UPLC BEH Phenyl column (100 mm \times 2.1 mm, 1.7 μ m, Waters), an Acquity UPLC photodiode array detector (PDA). The mobile phase was a mixture of acetonitrile and 5 mmol/L hydrochloric acid aqueous solution (90/10, v/v) [33]. The PDA detector was set at 210 nm. Data collection and management was performed by Empower 2 build 2154 software (Waters).

2.5. Partition coefficient and extraction efficiency of MAA

The partition coefficient of MAA between IL-rich phase and water-rich phase is determined according to Eq. (1),

$$P_{IL/W} = \frac{[MAA]_{IL}}{[MAA]_W} \quad (1)$$

where $P_{IL/W}$ represents the partition coefficient of MAA between IL-rich phase and water-rich phase, $[MAA]_{IL}$ and $[MAA]_W$ is the mass fraction of MAA in the IL-rich and water-rich phases, respectively.

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