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Short communication

Leaching separation of taurine and sodium sulfate solid mixture using ionic liquids

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Abstract

The solubilities of taurine (2-aminoethanesulfonic acid ($H_2NCH_2CH_2SO_3H$)) and sodium sulfate in a series of room temperature ionic liquids were examined, and a novel and greener separation method combined with chlorinated dialkylimidazolium ionic liquid as leaching reagent and organic solvent as precipitating reagent was developed. Using such process, selective separation of taurine from solid mixture containing large amount of sodium sulfate could be realized with 67–98.5% of single separation yield. The recycling of ionic liquid and organic solvent used in this separation process is possible.

Keywords: Ionic liquid; Leaching separation; Taurine; Solubility; Sodium sulfate

1. Introduction

The selective separation of organic and inorganic compounds is a crucial issue in the chemical industry. Leaching separation is considered to be an important technology in the development of separation processes [1,2]. Generally, traditional leaching separation, however, employs either organic solvents or water as leaching reagents. If, in some cases, desired substance could not be dissolved into conventional organic solvents or water, or could not be recovered from a leaching reagent, separation yield is poor. Moreover, organic solvents are generally volatile, toxic and flammable. Therefore, to search and establish more effective and clean leaching reagents and corresponding method is worth exploring for the development of new separation processes.

Taurine, i.e. 2-aminoethanesulfonic acid (H_2NCH_2-CH_2SO_3H), is the most abundant free amino acid, which is needed in human organs including heart, brain and liver, and is involved in a number of crucial physiological processes. Recently taurine is considered to play an important role during fetal life and appears to be vital for the growth of fetus in general and for development of central nervous system of fetus in particular. Therefore, it was widely used as food additive in daily food industry. Commercial taurine is currently produced through following two-step reactions in industry [3]:

$$H_2NCH_2CH_2OH + SO_3 \rightarrow H_2NCH_2CH_2OSO_3H$$

$$H_2NCH_2CH_2OSO_3H + Na_2SO_3 \rightarrow H_2NCH_2CH_2SO_3H + Na_2SO_4$$

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In the second reaction, sodium sulfate must be removed from the resulted solid mixture of sodium sulfate and taurine in order to obtain a pure taurine. Taurine is insoluble in the most common organic solvents, and its temperature of melting point (ca. 328 °C) and decomposition (315 °C) are very closed. Therefore, distillation to separate taurine from sodium sulfate containing mixture is unrealistic. Moreover, simple recrystallization method was almost impracticable because of solubility of taurine in water is not considerably different from that of sodium sulfate. So far, the separation of taurine and sodium sulfate could be achieved through two methods: (1) reiterative recrystallization in water; and (2) reiterative electrodialysis. These two methods suffer from relatively low taurine yield (less than 75%), higher energy consumption and complicated operations.

Room temperature ionic liquids, as a new kind of solvents and reaction media with unique physicochemical properties, have been attracted growing interests, and many catalytic reactions proceeded in ionic liquids were reported with excellent performance [4–11]. Although room temperature ionic liquids as novel media for “clean” extraction were reported [12–16] recently, the potentials of room temperature ionic liquids for the separation processes, however, are far from being recognized.

Within our continuing efforts to explore the applications of room temperature ionic liquids as novel ‘green’ liquid media, the solubilities of taurine and sodium sulfate in a series of room temperature ionic liquids were examined, and a novel separation method combined with ionic liquid as leaching reagent and organic solvent as precipitating reagent was developed. Selective separation of taurine from solid mixture containing large amount of sodium sulfate was conducted using such process in this report.

2. Experimental section

2.1. Materials and apparatus

All inorganic and organic chemicals were analytical grade and were used as received unless noted otherwise. The ^{1}H NMR spectra were taken in water-d_2 (∼0.1 M solutions) with an Inova-400 MHz NMR spectrometer. Proton chemical shifts are reported downfield from DSS. IR spectra were reported as films between NaCl plates with a Browk H120 FTIR spectrophotometer. The atomic absorption spectra were taken in deionized water with a HITACHI 180–80 model AAS instrument.

2.2. Synthesis of ionic liquids

Room temperature ionic liquids, 1-propyl-3-methylimidazolium chloride ([C_3MIm]Cl), 1-butyl-3-methylimidazolium chloride ([C_4MIm]Cl), 1-amyl-3-methylimidazolium chloride ([C_5MIm]Cl), 1-hexyl-3-methylimidazolium chloride ([C_6MIm]Cl), 1-propyl-3-methylimidazolium bromide ([C_3MIm]Br), 1-butyl-3-methylimidazolium bromide ([C_4MIm]Br), 1-amyl-3-methylimidazolium bromide ([C_5MIm]Br), 1-hexyl-3-methylimidazolium bromide ([C_6MIm]Br), 1-butyl-3-methylimidazolium iodide ([C_4MIm]I), 1-butyl-3-methylimidazolium hexafluorophosphate ([C_4MIm] PF_6) and 1-butyl-3-methylimidazolium tetrafluoroborate ([C_4MIm]BF_4) were synthesized according to previous paper with slight modifications [17,18]. The purity of prepared ionic liquids was characterized with FTIR and NMR, and satisfactory results were obtained.

2.3. Solubility measures in ionic liquids

The solubilities were determined by visual observation of the dissolutions of taurine or sodium sulfate in ionic liquids at constant temperature. For example, 0.1 g taurine was added into 10.0 g ionic liquid contained in a 25 ml round-bottomed flask equipped with a magnetic stirrer at constant 80 °C in each time. If taurine was dissolved completely, the addition of taurine would be repeated. The taurine solubility in ionic liquids would be determined when the taurine added could not be dissolved completely after the process of dissolution proceeded for 12 h. Because of the hygroscopic property of the ionic liquids, the flask inlet was blocked during dissolution. The sodium sulfate solubility in ionic liquids was also measured with the same method.

2.4. Leaching separation of taurine from sodium sulfate containing solid mixture

Typical separation procedures were as follows: 4 g solid mixture of taurine and sodium sulfate, in which sodium sulfate content was between 57 to 95 wt.%, was added into a 25 ml round-bottomed flask containing 12 g ionic liquid. The dissolving process proceeded with stirring at 80 °C for 40 min. After filtration to remove the insoluble sodium sulfate at room temperature, a clear percolate (ionic liquid + taurine) with lower melting point was obtained. Taurine solid could be recovered after excessive amount of organic solvent (the volume ratio of organic solvent to ionic liquid are 4–6), as a "precipitant" was added into the percolate to "precipitate" the taurine, and then by filtration to remove the percolate of organic solvent containing ionic liquid. The ionic liquid could be recovered and re-used after removing organic solvent from the ionic liquid by distillation and further vacuum treatment. The residual sodium sulfate in the resulted taurine was estimated through analyzing the content of sodium ion with 3520 ICP AES instrument (ARL Co., USA).

3. Results and discussion

3.1. Examination of solubilities of Na_2SO_4 and taurine in various ionic liquids

Firstly, the solubilities of taurine and sulfate in a series of ionic liquids with different cationic or anionic ions were tested at 80 °C (Table 1 and Fig. 1). In the widely used $[C_4MIm]BF_4$ and $[C_4MIm]PF_6$ ionic liquids, the solubilities of taurine and sodium sulfate were close to or even less than 1 g/100 g. When the anion of ionic liquid was changed from BF_4^- or PF_6^- into I^-, Br^- or Cl^-, the sodium sulfate solubility was still less than 1 g/100 g, the taurine solubility, however, was increased from 1, 10 to 21 g/100 g in turn, indicating that stronger electron-negativity Cl^- as anion of 1-butyl-3-methylimidazolium ionic liquid is more favorable for the taurine to be dissolved. This may be related to the formation of hydrogen bond between Cl^- and N–H in the taurine, which would result in the increase of taurine solubility in the chlorinated 1-butyl-3-methylimidazolium ionic liquid. As expected, cation ions in the ionic liquids have also some impact on the taurine solubility, and it can be seen (Fig. 1) that taurine solubility would increase with decrease of C number of alkyl group attached to imidazolium although such influence on the taurine solubility was relatively less remarkable. This may be related to the lipophilicity of the ionic liquids, i.e. the ionic liquid lipophilicity increases with increase of C number of alkyl group attached to imidazolium, and the higher ionic liquid lipophilicity is, the lower taurine solubility is. It is worth to note that low solubility of sodium sulfate were observed in all the ionic liquids employed in this work. Therefore, separation of taurine from sodium sulfate containing mixture using chlorinated $[C_nMIm]Cl$ ($n = 3$–5) as leaching reagent is possible, and $[C_3MIm]Cl$ possess the highest solubility for taurine and low enough solubility for sodium sulfate.

3.2. Taurine isolation from solid mixtures containing sodium sulfate

Based on the results as shown above, total taurine isolation from a solid mixture containing 57 wt.% of sodium sulfate was further examined with $[C_3MIm]Cl$ to $[C_5MIm]Cl$ ionic liquids. After sodium sulfate and taurine solid mixture was added into the chlorinated dialkylimidazolium ionic liquids and stirred at 80 °C for 40 min, white solid, i.e. sodium sulfate as precipitate was gradually separated out. With a simple filtration to

Table 1
Solubilities of Na_2SO_4 and taurine in various liquid media

Solvents	Temperature (°C)	Na_2SO_4 (g/100 g)	Temperature (°C)	Taurine (g/100 g)
$[C_4Mim]PF_6$	80	<1	80	<1
$[C_4Mim]BF_4$	80	<1	80	<1
$[C_4Mim]Cl$	80	Insoluble[a]	80	21.00
Water	25	21.87	25	10.48
Water	75	43.78	70	33.05
Ethanol	25	Insoluble[a]	25	Insoluble[a]

[a] Reference [19].

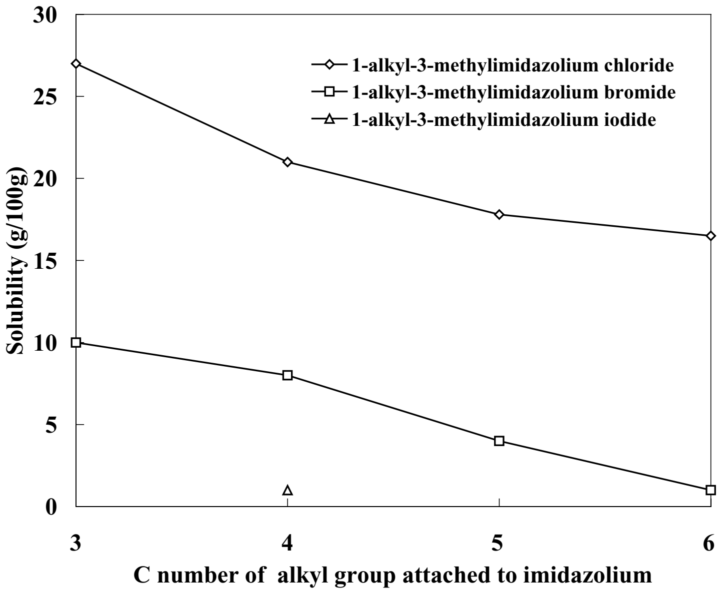

Fig. 1. Solubilities of taurine in different halogenated 1-alkyl-3-methylimidazolium ionic liquids.

remove the precipitated sodium sulfate at room temperature, a percolate of [C_nMIm]Cl (n = 3–5) and taurine liquid mixture was obtained. Interestingly, for [C_3MIm]Cl, a liquid of [C_3MIm]Cl and taurine mixture with low melting point could be formed (e.g. the melting point of pure [C_3MIm]Cl is ca. 76 °C, while melting point of [C_3MIm]Cl containing ca. 15 wt.% of taurine was lower than -30 °C.

Since taurine is not soluble in the most of conventional organic solvents, it is, therefore, impossible to recover taurine from the ionic liquid through liquid–liquid extraction. Fortunately, taurine dissolved in the ionic liquid could be easily separated out when a suitable organic solvent with excessive amount (the volume ratio of organic solvent to ionic liquid are 4–6), in which taurine is not soluble while the chlorinated dialkylimidazolium ionic liquids are well soluble, was added into the [C_nMIm]Cl (n = 3–5) and taurine liquid mixture at room temperature. Desired taurine crystallite could be obtained by simple filtration to remove the organic solvent containing the ionic liquid.

A series of organic solvents, that are mutually soluble with [C_nMIm]Cl (n = 3–5), were further examined to precipitate taurine dissolved in the ionic liquids, and the results are listed in Table 2. All the shot-chain alcohols, i.e. methanol, ethanol and *n*-propanol, were effective for the precipitation procedure. A 96–98.5% separation yield of taurine was achieved using [C_4MIm]Cl ionic liquid as leaching reagent when the shot-chain alcohols were employed as “precipitating” reagent, and ethanol, in addition to its high efficiency for precipitating, was ideal choice since it is relatively cheap and environmentally benign. As to nitromethane and acetonitrile as precipitating reagent, poor separation yields were observed. This may be attributed to the relatively high solubility of taurine in both of nitromethane and acetonitrile. It is worthy noted that the ionic liquids and ethanol are

Table 2
Effects of organic solvents on the separation yield of taurine

Organic solvent	CH_3OH	CH_3CH_2OH	$CH_3CH_2CH_2OH$	CH_3NO_2	CH_3CN
Separation yield (%)	96.0	98.5	97.6	74.5	71.0
Sodium sulfate content (mg/g)	1.65	1.01	0.87	2.16	2.96

Table 3
Results of separation of taurine from chlorinated 1-alkyl-3-methylimidazolium ionic liquids

Ionic liquid	Na_2SO_4 content before separation (g/100 g)	Separation yield (%)	Na_2SO_4 content after separation (g/100 g)
$[C_3Mim]Cl$	57.1	98.5	0.10
$[C_4Mim]Cl$	57.1	98.5	0.10
$[C_5Mim]Cl$	57.1	98.2	0.09
$[C_3Mim]Cl$[a]	57.1	97.0	0.12

[a] Re-used for the fifth time.

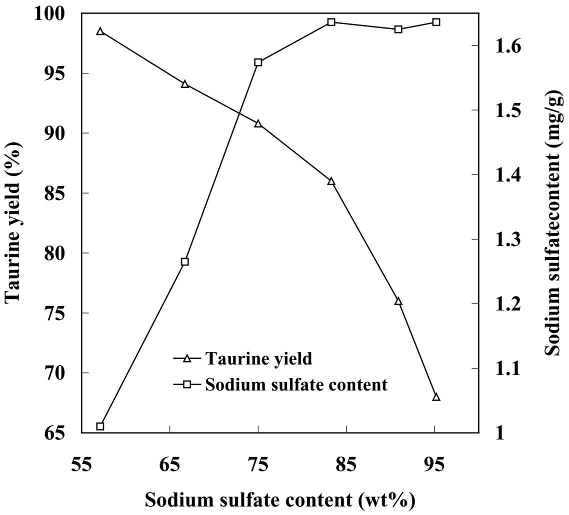

Fig. 2. The influence of Na_2SO_4 content in the mixture of Na_2SO_4 + taurine on taurine yield and residual Na_2SO_4 content.

now considered to be clean solvents. Therefore, this leaching separation of taurine from large sodium sulfate containing mixture should be an environmentally benign method.

For the comparison, $[C_3MIm]Cl$ and $[C_5MIm]Cl$ ionic liquids as leaching reagent were also tested using ethanol as precipitating reagent (Table 3). Because the amount of taurine charged in each leaching was less than that of solubilities that $[C_3MIm]Cl$ or $[C_5MIm]Cl$ possessed, the difference in taurine separation yields between $[C_3MIm]Cl$ and $[C_5MIm]Cl$ was small. Sulfate content in taurine could be greatly decreased from 5.7 g/100 g before separation to ca. 0.1 g/100 g through a single treatment of leaching and separation. ASS analysis showed that the residual sodium content in the separated taurine crystallite was less than 0.03 wt.%. This may indicate that the residual sodium sulfate content in the separated taurine should be less than 0.1 wt.%.

3.3. *Influence of sodium sulfate content on the yield and possible recycling of ionic liquid*

Using $[C_3MIm]Cl$ and ethanol as leaching and “precipitating” reagents, the influence of sodium sul-

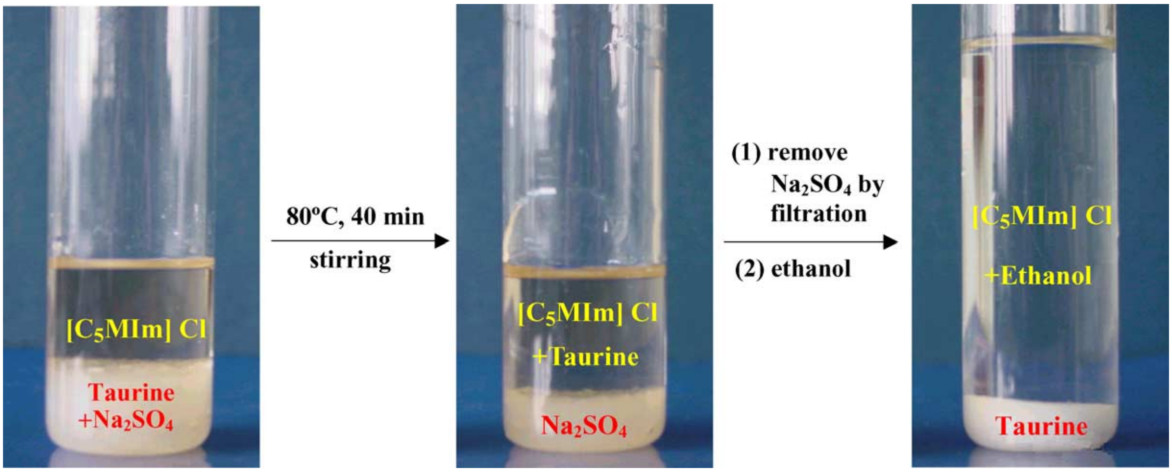

Fig. 3. Total separation process of leaching separation of taurine from solid mixture containing large amount of Na_2SO_4 using $[C_5MIm]Cl$ as leaching reagent and ethanol as precipitating reagent.

fate content in the mixture of sodium sulfate and taurine on the recovery yield for taurine was further examined (Fig. 2). It can be seen that the recovery yield of taurine would decrease with increasing the sodium sulfate content, however, 67% of taurine yield could still be achieved even if the sulfate content in the mixture was as high as 95 wt.%, indicating that the ionic liquid as leaching reagent is highly efficient for the separation of taurine from the sodium sulfate containing mixture. On the other hand, the residual sodium sulfate in the separated taurine would initially increase remarkably as the sodium sulfate content was increased from 57 to 85%, however, it was only increased from ca. 1.1 to 1.6 mg/g as the initial sodium sulfate content in the solid mixture was reached to 95 wt.%.

The recycling of ionic liquid as leaching reagent was also tested since the ionic liquid could easily be recovered from ethanol by distillation. A 97% of separation yield was still maintained after the [C_3MIm]Cl was re-used for five times (Table 3), indicating the recycling of ionic liquid used in this separation process is possible. Since organic solvent used as “precipitating” reagent such as ethanol was also recoverable, this method should be environmentally benign, and such total separation process is shown in Fig. 3.

4. Conclusion

In summary, taurine solubility in a series of ionic liquids was preliminarily investigated, and selective separation of taurine from large amount of sodium sulfate containing solid mixture was successfully performed using chlorinated dialkylimidazolium ionic liquids as leaching reagent and then using shot-chain alcohols, i.e. methanol or ethanol as “precipitating” reagent with 67–98.5% of single separation yield for taurine. The recycling of ionic liquid in this separation process is possible. The potentials of ionic liquids in the application of separation processes was further revealed, and to our best knowledge, it is the first time that selective separation of taurine from sodium sulfate containing solid mixture was reported using chlorinated dialkylimidazolium ionic liquids. This method can be useful for the practical applications.

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