Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Recovery of Furfural from Aqueous Solution by Ionic Liquid Based Liquid-Liquid Extraction

Yuanchao Pei[a]; Kun Wu[b]; Jianji Wang[b]; Jing Fan[b]
[a] College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, Gansu, P. R. China [b] School of Chemistry and Environmental Science, Henan Normal University, Xinxiang, Henan, P. R. China

To cite this Article Pei, Yuanchao , Wu, Kun , Wang, Jianji and Fan, Jing(2008) 'Recovery of Furfural from Aqueous Solution by Ionic Liquid Based Liquid-Liquid Extraction', Separation Science and Technology, 43: 8, 2090 — 2102
To link to this Article: DOI: 10.1080/01496390802064018
URL: http://dx.doi.org/10.1080/01496390802064018

Separation Science and Technology, 43: 2090–2102, 2008
Copyright © Taylor & Francis Group, LLC
ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390802064018

Recovery of Furfural from Aqueous Solution by Ionic Liquid Based Liquid–Liquid Extraction

Yuanchao Pei,[1] Kun Wu,[2] Jianji Wang,[2] and Jing Fan[2]
[1]College of Chemistry and Chemical Engineering, Lanzhou University,
Lanzhou, Gansu, P. R. China
[2]School of Chemistry and Environmental Science, Henan Normal University,
Xinxiang, Henan, P. R. China

Abstract: Liquid–liquid extraction with imidazolium based ionic liquids ([C_4mim][PF_6], [C_6mim][PF_6], and [C_8mim][PF_6]) is proposed for the separation of furfural or 5-methylfurfural from aqueous solution. Factors affecting the extraction of furfural or 5-methylfurfural have been studied. It was shown that the extraction equilibria can be achieved within 30 min and the process was less affected by the factors such as volume ratio and feed concentration. The partition coefficients of furfural and 5-methylfurfural decreased with increasing temperature. [C_6mim][PF_6] was found to have the best extraction ability among the three ionic liquids studied. Presence of small amount of NaCl or Na_2SO_4 in the aqueous phase results in the considerable increase in the partition coefficients of furfural because of the competitive hydration of the salts with furfural. A thermodynamic study revealed that the extraction process was driven mainly by hydrophobic interactions. Further experimental results indicated that furfural can be separated selectively from aqueous furfural/acetic acid mixtures.

Keywords: Acetic acid; Furfural; Ionic liquid; Liquid–liquid extraction; 5-methylfurfural

INTRODUCTION

Biomass has received a great deal of attention both as an energy source and as a renewable raw material in the past few years. Processing of

Received 3 October 2007; accepted 21 January 2008.

Address correspondence to Jianji Wang, School of Chemistry and Environmental Science, Henan Normal University, Xinxiang, Henan 453007, P. R. China. Tel.: + 86-373-3325805; Fax: + 86-373-3326445; E-mail: jwang@henannu.edu.cn

biomass can broaden the options of the chemical industry giving it more flexibility and a broader range of products. The utilization of biomass, especially in the case of unutilized agricultural and forest residues rather than fossil fuels, could offer more environmentally acceptable processes and could aid in conserving the limited supplies of fossil fuels, which could in turn lead to a sustainable global ecosystem.

Furfural usually acts as a good raw material for petroleum refining industries and chemical industries and as an intermediate product in synthesizing chemical products such as pharmaceutical precursors, nylons, lubricants, adhesives, and plastics (1). The main advantage of using furfural is that it can be made from renewable agricultural resources and the residues from forest products. Furfural is mainly manufactured by acid hydrolysis of pentosan-containing plants or their waste products (2). This process produces diluted aqueous solutions of furfural and acetic acid. Common separation methods for furfural include distillation (3–5), solid adsorption (6) and extraction by suitable solvents (7–12). Distillation of aqueous furfural solution is complicated by the formation of the azeotrope which contains about 36% of furfural at the atmospheric pressure (5). Pure furfural is obtained in the second distillation step. The consumption of energy for such process is high. For the adsorptions with solid materials such as charcoal, wood chips, and ion exchangers, preparation of mechanically stable packing for efficient adsorption column is difficult and also desorption of the furfural from these materials is not easy. Alcohols (7), chlorinated hydrocarbons (10,11), trioctylphosphinoxide, and ethyl acetate (12) are often used to extract furfural produced during acid hydrolysis of biomass. Unfortunately, most of these organic solvents are volatile, flammable and toxic, and result in severe environmental pollution and health problem. Supercritical carbon dioxide (13,14), as a clean solvent, was also used for the extraction of furfural from aqueous solutions. However, this process is very expensive and would increase the cost of furfural manufacture. Recently, reverse osmosis membranes (15) and flat sheet hydrophobic polyurethaneurea membranes (16) have been used to separate furfural from aqueous solutions. It is found that furfural can permeate selectively these membranes with high separation factor.

In recent years, people are increasingly interested in using ionic liquids (ILs) for chemical synthesis, biocatalytic transformation, electrochemical device designs, and separation process (17–23), due to their "green" characteristics. In this work, imidazolium based ionic liquids 1-butyl-3-methylimidazolium hexafluorophosphate ($[C_4mim][PF_6]$), 1-hexyl-3-methylimidazolium hexafluorophosphate ($[C_6mim][PF_6]$), and 1-octyl-3-methylimidazolium hexafluorophosphate ($[C_8mim][PF_6]$) have been used, for the first time, to remove furfural or 5-methylfurfural from aqueous solutions. Effect of equilibration time, volume of aqueous phase, feed concentration, temperature, structure of ILs, and type of salts on the extraction process have been investigated in detail. Separation of furfural from aqueous acetic acid solutions was also studied. In addition, thermodynamic properties for the transfer of furfural from aqueous to ILs phases have been determined to provide the basis for the interactions between ILs and furfural.

EXPERIMENTAL

Materials

Furfural and 5-methylfurfural were purchased from Sigma Aldrich (St. Loius, MO, USA), and redistilled under vacuum before use. 1-Bromobutane, 1-bromohexane, and 1-bromooctane were obtained from Alfa Aesar (Ward Hill, MA, USA). 1-Methylimidazolium was purchased from Linhai Kaile Chem. Co. (Zhejiang, China). 1-Methylimidazolium and alkyl halides were distilled at reduced pressure before use. All other chemicals were analytical grade and used without further purification. Water used in the research was always freshly deionized and distilled before use.

Synthesis of Ionic Liquids

[C_4mim][PF_6], [C_6mim][PF_6], and [C_8mim][PF_6] ionic liquids were prepared and purified according to the methods described previously (24, 25). ^{1}H-NMR and ^{13}C-NMR spectra data of these ILs were determined by using a Bruker AV-400 Spectrometer, and they were found to be in good agreement with those reported in literature (26–28).

Experimental Methods

Aqueous furfural or 5-methylfurfural solutions were prepared by directly dissolving the chemicals into deionized water. Extraction experiments were performed in a water bath at the temperature of $25 \pm 0.1^\circ$C controlled by a DC-2006 low temperature system (Shanghai Hengping Instrument Factory). A preliminary study showed that furfural concentration had little influence on the extraction. Therefore, $0.1\,\mathrm{mol \cdot L^{-1}}$ was chosen for further studies because this concentration was close to that used in the industrial process. 5.0 mL of such aqueous solution of furfural was contacted with 1.0 mL of a prepared IL. The phase-contacting experiments were carried out carefully in stoppered glass test tubes. The extraction system was vigorously stirred with magnetic stirrers for 30 min.

The phase separation occurred quickly after cessation of stirring process. However, a XYJ-802 centrifuge (Jiangsu Medical Instrument Factory) operated at 2000 rpm was still used to run for a period of 5 min in each test to ensure a complete phase separation. Then the sample was collected from the top aqueous phase and diluted for analyses.

Before and after each extraction, the concentration of furfural or 5-methylfurfural in the aqueous solution was determined with a Shanghai 752 UV-vis spectrophotometer according to the literature method (6). Partition coefficients ($P_{IL/W}$) of the furfural or 5-methylfurfural between the ILs and aqueous phases were calculated by using the equation

$$P_{IL/W} = (C_i - C_f)V_{aq}/(C_f V_{IL}) \qquad (1)$$

where C_i and C_f represent the initial and final concentrations ($mol \cdot L^{-1}$) of furfural or 5-methylfurfural in an aqueous phase, and V_{aq} and V_{IL} are the volumes of aqueous and ILs phases, respectively. In the present work, a volume ratio of $V_{aq}/V_{IL} = 5/1$ was applied. The $P_{IL/W}$ values were measured in duplicate with uncertainties less than 2%.

RESULTS AND DISCUSSION

Effect of Equilibration Time and Phase Volume Ratio

In order to study the effect of equilibration time, the partition coefficients of furfural between [C_6mim][PF_6] and water were determined with the increase of equilibration time. It was shown that equilibration was achieved within 30 min or less. At 25°C, the partition coefficients of furfural were 15.3 and 15.8 at the equilibration time of 10 min and 30 min, respectively. There is no apparent change in the partition coefficients of furfural with the further increase of equilibration time. Therefore, 30 min of equilibration was used in all experiments.

The optimum extraction phase volume ratio is tested with a series of experiments. The results showed that the partition coefficients of furfural were not affected significantly by the volume ratio. To obtain the optimum partition coefficients and smallest amount of ionic liquids used, a volume ratio, 5:1, of an aqueous phase to an IL phase was selected for all the experiments.

Temperature Effect and the Transfer Thermodynamic Properties

To assess the temperature effect of the furfural or 5-methylfurfural extraction by ILs, a series of extraction experiments were performed at

15, 25, 35, 45, and 55°C, and the obtained $P_{IL/W}$ values are listed in Table 1. It can be seen that the extraction efficiency of furfural or 5-methylfurfural decreased with the increase of temperature.

From the viewpoint of thermodynamics, the extraction of furfural or 5-methylfurfural into a particular IL from the aqueous phase can be regarded as its transfer process from the aqueous phase to the IL phase. The Gibbs energy (ΔG_T^0) of such a transfer process at a given temperature can be calculated from the mole-fraction extraction equilibrium constant, K_x by using the following equation (25)

$$\Delta G_T^0 = -RT \ln K_x = -RT[\ln P_{IL/W} + \ln(V_{m,IL}/V_{m,W})] \tag{2}$$

where $V_{m,IL}$ and $V_{m,W}$ represent the molar volumes of ILs and water, respectively. The molar volumes of water at different temperatures can be calculated from the density data reported by Kell (29) and the molar mass of water. The density data for the tested ILs at different temperatures have been determined by using an Anton Paar DMA 60/602 digital densimeter in our previous work (25). The molar volumes for the ILs were calculated from these density data and the values of molar mass of ILs. If the transfer enthalpies (ΔH_T^0) for furfural are assumed to be constant over the short temperature range studied, their values can be calculated from the linear relationships between $\ln K_x$ and $1/T$ expressed as follows:

$$\ln K_x = -\frac{\Delta H_T^0}{RT} + \frac{\Delta S_T^0}{R} \tag{3}$$

The transfer enthalpies and transfer entropies for the furfural or 5-methylfurfural can be determined from the slopes ($-\Delta H_T^0/R$) and the intercept ($\Delta S_T^0/R$) of the plots. The obtained ΔG_T^0, ΔH_T^0, and $T\Delta S_T^0$ values along with the experimental $P_{IL/W}$ data are included in Table 1. It can be seen that all the values of ΔH_T^0 and ΔG_T^0 are negative whereas those of ΔS_T^0 are positive. These thermodynamic data suggest that these extraction processes are exothermic in nature and driven by entropy terms. This is the characteristic of hydrophobic interactions (30). Thus, thermodynamic study revealed that hydrophobic interactions are the main driving force for IL-based removal of the furfural or 5-methylfurfural from aqueous solutions.

Effect of Chemical Structure of the ILs

As can be seen from Table 1, the partition coefficients of furfural and 5-methylfurfural in the IL/aqueous systems follow the trend:

Table 1. Thermodynamic properties for the transfer of furfural and 5-methylfurfural from aqueous phase to the ionic liquids

	$[C_4mim][PF_6]$				$[C_6mim][PF_6]$				$[C_8mim][PF_6]$			
T (°C)	$P_{IL/W}$	ΔG_T^0 $(kJ \cdot mol^{-1})$	ΔH_T^0 $(kJ \cdot mol^{-1})$	$T\Delta S_T^0$ $(kJ \cdot mol^{-1})$	$P_{IL/W}$	ΔG_T^0 $(kJ \cdot mol^{-1})$	ΔH_T^0 $(kJ \cdot mol^{-1})$	$T\Delta S_T^0$ $(kJ \cdot mol^{-1})$	$P_{IL/W}$	ΔG_T^0 $(kJ \cdot mol^{-1})$	ΔH_T^0 $(kJ \cdot mol^{-1})$	$T\Delta S_T^0$ $(kJ \cdot mol^{-1})$
furfural												
15	15.0	−12.3	−5.8	6.5	16.2	−12.9	−4.2	8.7	14.8	−13.0	−2.9	10.1
25	14.1	−12.6		6.8	15.7	−13.3		9.1	14.0	−13.3		10.4
35	12.8	−12.8		7.0	14.7	−13.5		9.3	13.7	−13.7		10.8
45	11.8	−13.0		7.2	13.6	−13.8		9.6	13.0	−14.0		11.1
5-methylfurfural												
15	20.2	−13.0		5.4	24.9	−13.9		9.0	23.4	−14.1		11.4
25	19.3	−13.4		5.8	23.7	−14.3		9.4	22.9	−14.5		11.8
35	18.1	−13.7	−7.6	6.1	22.7	−14.7	−4.9	9.8	21.7	−14.9	−2.7	12.2
45	16.3	−13.9		6.3	21.1	−14.9		10.0	20.9	−15.3		12.6
55	13.1	−13.7		6.1	19.0	−15.1		10.2	20.4	−15.7		13.0

$P_{[C6mim][PF6]} > P_{[C8mim][PF6]} > P_{[C4mim][PF6]}$. The best extraction efficiencies are obtained by $[C_6mim][PF_6]$, which is not agreement with the hydrophobicity of ILs. Similar anomalous behavior of $[C_6mim]^+$ has been observed by other researchers for the polarity or melting point of ILs (31), and for the extraction of alkali metal cation or amino acids by ILs (24,26). At the moment, we can not have a reasonable explanation for such results.

Data in Table 1 revealed an interesting feature for the partition coefficients of furfural and 5-methylfurfural into a particular ionic liquid at the same condition: 5-methylfurfural > furfural. From the view point of chemical structure, 5-methylfurfural has a $-CH_3$ group more than furfural, and the $-CH_3$ group is hydrophobic in nature. So it seems appropriate to state that the hydrophobic groups increase the partition coefficients of furfural into ionic liquids. This result supports the above-mentioned conclusion that hydrophobic interactions are the main driving force for the extraction of furfural and 5-methylfurfural.

Effect of Salt Concentration

In the actual manufacture process, furfural presents along with different salts. To understand the effect of type and concentration of salts on extraction efficiency, furfural solution with different concentrations of NaCl or Na_2SO_4 were prepared and tested at neutral pH. The results of salt effect are shown in Figs. 1 and 2. It can be seen that the extraction efficiency of furfural increased significantly with the increase in concentrations of NaCl or Na_2SO_4. The ability of the salt effect follows the order: $Na_2SO_4 > NaCl$. Considering the fact that NaCl and Na_2SO_4 share a common cation but contain different anions, it is easy to see that the salt effect is related to the Gibbs energy of hydration of anions: SO_4^{2-} ($\Delta G_{hyd} = -1080\,kj \cdot mol^{-1}$) > Cl^- ($\Delta G_{hyd} = -340\,kj \cdot mol^{-1}$) (32). Therefore, the salt effect can be explained by the competitive hydration of the salt with furfural. In other words, NaCl and Na_2SO_4 hydrate more water molecules than furfural, resulting in the easy transfer of furfural from water to ILs phase.

Separation of Furfural from Aqueous Acetic Acid Solutions

In the actual manufacture process, acetic acid was produced along with furfural. In order to examine the selective extraction ability of the ILs, a mimic aqueous solution containing 5.0% of furfural and 2.0% of acetic acid was prepared and used for the selective extraction experiments. Figure 3 shows the partition coefficients of furfural and acetic acid in

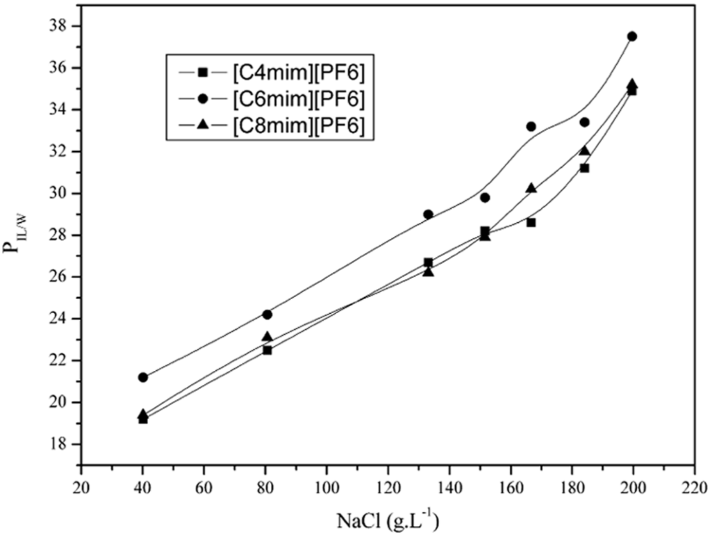

Figure 1. Effect of NaCl concentrations on the partition coefficients of furfural at 25°C.

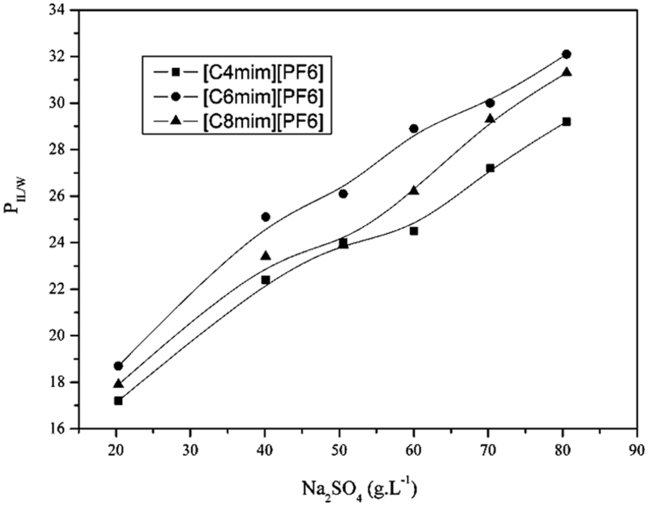

Figure 2. Effect of Na_2SO_4 concentrations on the partition coefficients of furfural at 25°C.

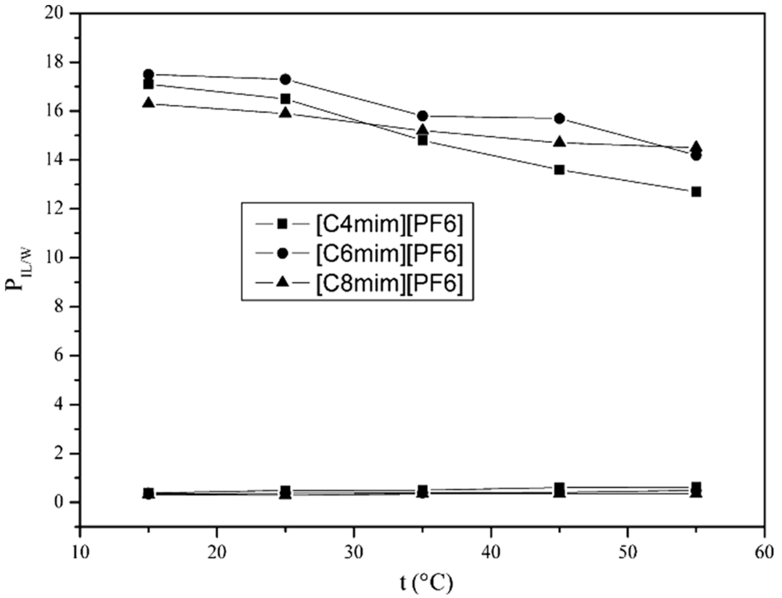

Figure 3. Partition coefficients of furfural and acetic acid between ionic liquids and water at different temperatures.

the aqueous furfural/acetic acid solutions at different temperatures. It can be seen that the partition coefficients of furfural are higher significantly than those of acetic acid. The separation factor can be around 50. This implies that furfural could be extracted efficiently from feed effluent by ILs without the interference of acetic acid.

Compared with Other Extracting Solvents

In this work, the ILs exhibited high extraction efficiency for furfural and 5-methylfurfural. For example, most of the partition coefficients of furfural are in the range of 15.0–16.2 at room temperature. In fact, about 76% of furfural and 83% of 5-methylfurfural can be extracted from aqueous solution into the ILs at room temperature. In Table 2, a comparison was made of the partition coefficients of furfural between the ILs and the conventional solvents (33). As can be seen, the partition coefficients of furfural into the conventional organic solvents are usually much lower than those into the ILs. More importantly, ionic liquids are nonvolatile and nonflammable, and this suggests that ionic liquids might potentially be the "green solvents". On the contrary, the conventional organic solvents for extraction of furfural, like straight

Table 2. Partition coefficients of furfural into the ILs and some conventional organic solvents from aqueous solutions at room temperature

$P_{IL/W}$							
1 ($C_4 \sim C_{10}$)	2 ($C_4 \sim C_6$)	3 (C_6)	4 ($C_4 \sim C_7$)	5 (C_5)	6 (C_6)	7 ($C_1 \sim C_2$)	ILs($C_4 \sim C_8$)
$0.71 \sim 0.3$	$4.41 \sim 2.11$	2.6	$8.4 \sim 5.5$	7.1	$6.2 \sim 4.1$	$14.7 \sim 2.3$	$15.0 \sim 16.2$

1. straight chain hydrocarbon; 2. alcohols; 3. isopropyl ether; 4. esters; 5. methyl isobutyl ketone; 6. benzene and derivatives; 7. halohydrocarbon.

chain hydrocarbon, halohydrocarbon, benzene and derivatives, etc., are toxic, flammable, and environmentally damaging to human health and the ecosystem. Therefore, compared with literature methods, the ionic liquid based extraction of furfural has the advantages of higher extraction efficiency, safety, and tunable properties of the ILs. These advantages make the ionic liquids have potential applications in practical liquid–liquid extraction process of furfural from aqueous solution.

Recovery of the Furfural and Reuse of the ILs

In the use of ILs for extraction process, recovery of the furfural and reuse of the ILs are of great importance. For the furfural/IL mixtures, furfural can be recovered from ILs via distillation at reduced pressure. ILs could then be reused for the next extraction step. However, this is not the economical method to recovery furfural in industry process. Alternative effective and economical methods need to be developed.

As mentioned above, furfural could be separated efficiently from water by using small quantities of ILs. However, the issue of the loss of very small amount of ILs into the aqueous phase should be addressed. At room temperature, the solubility of [C_4mim][PF_6], [C_6mim][PF_6], and [C_8mim][PF_6] in water is 1.88, 0.75, and 0.20 g/100 ml, respectively. Vijayaraghavan et al. (34) and Stepnowski (35) have successfully recovered the lost ILs from aqueous phase by using ion exchange resins. Recently, Li and co-workers (36) developed a highly efficient process for oxidative degradation of imidazolium based ionic liquids in hydrogen peroxide/acetic acid aqueous medium assisted by ultrasonic chemical irradiation. It is shown that more than 93% of ionic liquids can be degraded at 50°C within 12 h. However, the two methods are somewhat expensive. Therefore, low-cost methods for the recovery of ILs from water need to be developed. Another alternative method is the design of biodegradable ILs or more hydrophobic ILs. These studies are still ongoing in our laboratory.

The characteristics of IL-based furfural separation procedure could render ILs as a promising candidate for removal of furfural from water. However, a comprehensive study on the recovery of ILs with easily manageable and highly efficient procedures, and overall engineering cost analysis of IL-based furfural separation should be done.

CONCLUSION

A liquid–liquid extraction process using ionic liquids as extraction phase has been developed for the extraction of furfural and 5-methylfurfural from aqueous solutions. The results imply that the partition coefficients of the furfural are less influenced by the equilibration time, volume ratio of aqueous to ILs phases, feed concentration and pH of aqueous phase within the experimental error range. However, the partition coefficients of furfural or 5-methylfurfural could be improved considerably by the decrease of temperature and presence of a small amount of NaCl or Na_2SO_4 in the aqueous phase. Thermodynamic study revealed that the extraction process was driven mainly by hydrophobic interaction of furfural and with the ionic liquids. Among the ionic liquids used in this work, $[C_6mim][PF_6]$ has the best extraction ability. Based on the selective extraction experiment, it is found that furfural can be separated effectively from aqueous furfural/acetic acid solutions by the ILs. The results give promise of this novel route for the extraction of furfural. Taking into account the extraction ability of the ionic liquids, the recovery of furfural and reuse of ionic liquids, and the rational design of IL-based separation process is very essential.

ACKNOWLEDGEMENT

This work is supported financially by the National Natural Science Foundation of China under the grant contracts No. 20273019 and No. 20573034.

REFERENCES

1. Fele, L., Grilc, V. (2003) Separation of furfural from ternary mixtures. *J. Chem. Eng. Data*, *48* (3): 564.
2. Demirbas, A. (2006) Furfural production from fruit shells by acid-catalyzed hydrolysis. *Energy Sources, Part A*, *28* (2): 157.
3. Montane, D., Salvado, J., Torras, C., Farriol, X. (2002) High-temperature dilute-acid hydrolysis of olive stones for furfural production. *Biomass Bioenergy*, *22* (4): 295.

4. Vila, C., Santos, V., Parajó, J.C. (2003) Recovery of lignin and furfural from acetic acid–water–HCl pulping liquors. *Bioresour. Technol.*, *90* (33): 339.
5. Mordechai, P., John, R. Jr. Separation of furfural/middle distillate streams. U. S. Patent 4,982,051, January 1, 1991.
6. Gupta, P., Nanoti, A., Garg, M.O., Goswami, A.N. (2001) The removal of furfural from water by adsorption with polymeric resins. *Sep. Sci. Technol.*, *36* (13): 2835.
7. Cabezas, J.L., Barcena, L.A., Coca, J., Cockrem, M. (1988) Extraction of furfural from aqueous solutions using alcohols. *J. Chem. Eng. Data*, *33* (4): 435.
8. Zeitsch, K.J. (1999) Extractive condensation: A new separation process. *Ind. Eng. Chem. Res.*, *38* (10): 4123.
9. Roy Moulik, S.K., Khandelwal, P.K. (1989) Recovery of furfural from the prehydrolysis vapour vent condenstate from a dissolving pulp plant. *Research Industry*, *34*: 205.
10. Coca, J., Diaz, R. (1980) Extraction of furfural from aqueous solutions with chlorinated hydrocarbons. *J. Chem. Eng. Data*, *25* (1): 80.
11. Sunder, M.S., Prasad, D.H.L. (2003) Phase equilibria of water + furfural and dichloromethane + *n*-Hexane. *J. Chem. Eng. Data*, *48* (2): 221.
12. Liu, J.F., Yi, P.G., Chen, A.G. (2000) Selecting for solvent and equipment to separate furfural from improved sulfuric acid catalytic method. *Chem. Ind. Eng.*, (in Chinese) *17* (5): 303.
13. Gamse, T., Marr, R., Froschl, F., Siebenhofer, M. (1997) Extraction of furfural with carbon dioxide. *Sep. Sci. Technol.*, *32* (1–4): 355.
14. Sako, T., Sugeta, T., Nakazawa, N., Otake, K., Sato, M., Ishihara, K., Kato, M. (1995) High-pressure vapor-liquid and liquid–liquid equilibria for systems containing supercritical carbon dioxide, water and furfural. *Fluid Phase Equilib.*, *108* (1–2): 293.
15. Sagehashi, M., Nomura, T., Shishido, H., Sakoda, A. (2007) Separation of phenols and furfural by pervaporation and reverse osmosis membranes from biomass – superheated steam pyrolysis-derived aqueous solution. *Bioresour. Technol.*, *98* (10): 2018.
16. Ghosh, U.K., Pradhan, N.C., Adhikari, B. (2007) Separation of furfural from aqueous solution by pervaporation using HTPB-based hydrophobic polyurethaneurea membranes. *Desalination*, 208 (1–3): 146.
17. Rogers, R.D.; Seddon, K.R. (2002) *Ionic Liquids: Industrial Applications to Green Chemistry*. ACS Symposium Series, No. 818; American Chemical Society: Washington DC, U.S.A.
18. Rogers, R.D.; Seddon, K.R. (2005) *Ionic Liquids IIIA: Fundamentals, Progress, Challenges, and Opportunities: Properties and Structure*. ACS Symposium Series, No. 901; American Chemical Society: Washington DC, U.S.A.
19. Wasserscheid, P.; Welton, T. (2003) *Ionic Liquids in Synthesis*, Wiley-VCH: Weinheim, Gremany.
20. Rantwijk, F., Lau, R.M., Sheldon, R.A. (2003) Biocatalytic transformations in ionic liquids. *Trends Biotechnol.*, *21* (3): 131.

21. Buzzeo, M.C., Evans, R.G., Compton, R.G. (2004) Non-haloaluminate room-temperature ionic liquids in electrochemistry – A review. *Chem. Phys. Chem.*, *5* (8): 1106.
22. Pandey, S. (2006) Analytical applications of room-temperature ionic liquids: A review of recent efforts. *Anal. Chim. Acta*, *556* (1): 38.
23. Liu, J., Jonsson, J.A., Jiang, G. (2005) Application of ionic liquids in analytical chemistry. *Trends Anal. Chem.*, *24* (1): 20.
24. Wang, J.J., Pei, Y.C., Zhao, Y., Hu, Z.G. (2005) Recovery of amino acids by imidazolium based ionic liquids from aqueous media. *Green Chem.*, *7* (4): 196.
25. Pei, Y.C., Wang, J.J., Xuan, X.P., Fan, J., Fan, M.H. (2007) Factors affecting ionic liquids based removal of anionic dyes from water. *Environ. Sci. Technol.*, *41* (14): 5090.
26. Chun, S., Dzyuba, S.V., Bartsch, R.A. (2001) Influence of structural variation in room-temperature ionic liquids on the selectivity and efficiency of competitive alkali metal salt extraction by a crown ether. *Anal. Chem.*, *73* (15): 3737.
27. Huddleston, J.G., Visser, A.E., Reichert, W.M., Willauer, H.D., Broker, G.A., Rogers, R.D. (2001) Characterization and comparison of hydrophilic and hydrophobic room temperature ionic liquids incorporating the imidazolium cation. *Green Chem.*, *3* (4): 156.
28. Suarez, P.A.Z., Dullius, J.E.L., Einloft, S., de Souza, R.F., Dupont, J. (1996) The use of new ionic liquids in two-phase catalytic hydrogenation reaction by rhodium complexes. *Polyhedron*, *15* (7): 1217.
29. Kell, G.S. (1975) Density, thermal expansivity, and compressibility of liquid water from 0.deg. to 150.deg. Correlations and tables for atmospheric pressure and saturation reviewed and expressed on 1968 temperature scale. *J. Chem. Eng. Data*, *20* (1): 97.
30. Bianco-Peled, H., Gryc, S. (2004) Binding of amino acids to "smart" sorbents: Where does hydrophobicity come into play? *Langmiur*, *20* (1): 169.
31. Carmichael, A.J., Seddon, K.R. (2000) Polarity study of some 1-alkyl-3-methylimidazolium ambient-temperature ionic liquids with the solvatochromic dye, nile red. *J. Phys. Org. Chem.*, *13* (10): 591.
32. Marcus, Y. (1991) Thermodynamics of solvation of ions. *J. Chem. Soc. Faraday Trans.*, *87* (18): 2995.
33. Zhang, Y.M., Li, K.H., Huang, H.J. (1991) Study on solvent extraction processes for furfural separation. *Chem. Ind. Forest Products*, (in Chinese) *11* (3): 231.
34. Vijayaraghavan, R., Vedaraman, N., Surianarayanan, M., Macfarlane, D.R. (2006) Extraction and recovery of azo dyes into an ionic liquid. *Talanta*, *69* (5): 1059.
35. Stepnowski, P. (2005) Solid-phase extraction of room-temperature imidazolium ionic liquids from aqueous environmental samples. *Anal. Bioanal. Chem.*, *381* (11): 189.
36. Li, X.H., Zhao, J.G., Li, Q.H., Wang, L.F., Tsang, S.C. (2007) Ultrasonic chemical oxidative degradations of 1,3-dialkylimidazolium ionic liquids and their mechanistic elucidations. *Dalton Trans.*, (19): 1875.