Journal of Chromatography A, 1217 (2010) 7638–7641

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Microwave-assisted separation of ionic liquids from aqueous solution of ionic liquids

Sung Ho Ha [a], Ngoc Lan Mai [b], Yoon-Mo Koo [a,b,*]

[a] Center for Advanced Bioseparation Technology, Inha University, Incheon 402-751, South Korea
[b] Department of Biological Engineering, Inha University, Incheon 402-751, South Korea

ARTICLE INFO

Article history:
Received 17 September 2010
Received in revised form 2 October 2010
Accepted 5 October 2010
Available online 11 October 2010

Keywords:
Ionic liquids
Separation
Microwave irradiation
Mixture
Distillation

ABSTRACT

Microwave-assisted separation has been applied to recover ionic liquid (IL) from its aqueous solution as an efficient method with respect to time and energy compared to the conventional vacuum distillation. Hydrophilic ILs such as 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF_4]), 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([Bmim][TfO]) and 1-ethyl-3-methylimidazolium methylsulfate ([Emim][MS]) could be recovered in 6 min from the mixture of ILs and water (1:1, w/w) under microwave irradiation at constant power of 10 W while it took at least 240 min to obtain ILs containing same water content (less than 0.5 wt%) by conventional vacuum oven at 363.15 K with 90 kPa of vacuum pressure. Energy consumptions per gram of evaporated water from the homogeneous mixture of hydrophilic ILs and water (1:1, w/w) by microwave-assisted separation were at least 52 times more efficient than those in conventional vacuum oven. It demonstrated that microwave-assisted separation could be used for complete recovery of ILs in sense of time and energy as well as relevant purity.

1. Introduction

Ionic liquids (ILs) composed of organic cations and appropriate anions have received much interest in recent years as environmental benign sustainable solvents for chemical reactions and processes since ILs have many favorable properties including negligible vapor pressure, non-flammability, good thermal stability with wide liquid range [1–4]. Moreover, they can be tailored for a specific application by the right choice of cation and anions [3,6]. Due to these unique properties, ILs are considered as promising solvents in a wide field of applications including organic catalysis, biocatlysis, extraction, biomass processing and engineering fluids [5–14]. However, the big challenge for the industrial applications of ILs such as reaction media for (bio)chemical reactions, extraction solvents for liquid–liquid extraction and entrainers for extractive distillation resides in the economics of ILs use.

Since ILs usually exist as mixtures with solvents in many applications, the economic feasibility can be achieved by recycling them. When ILs make a separate phase from solvents, ILs can be easily recovered by simple decantation or a magnetic field [15–17]. However, it is not easy to separate pure ILs from a homogeneous mixture of ILs and solvents. Considering non-volatility of ILs, evaporation is one of the possible processes for the recovery of ILs from the mixture. However, conventional evaporation is an energy-intensive and time-consuming method for the removal of water or organic solvents and furthermore may not be practical for the mixture where ILs are the major component.

The use of microwave irradiation has become as a popular tool in modern chemistry as a source of energy [18,19]. Under microwave irradiation, the transfer of energy from microwaves to the substance occurs via two mechanisms, specifically by dipole rotation and ionic conduction which generates ionic motion present in a reaction medium. One advantage of this technique is that high reaction temperature can be rapidly achieved by excitation of polar molecules (via dipole rotation) or ions (via ionic conduction) in a microwave field. Therefore, dramatically reduced reaction times from hours to minutes with a significant increase in product yields and purities are generally possible [20,21]. From the perspective of microwave chemistry, ILs have several key properties to be exploited including high polarity (around that of methanol) and non-volatility. Using ILs, temperature above 200 °C can be easily reached within a few seconds [22]. As a result, the advantage of efficient microwave heating and green properties of ILs have been combined in performing various reactions [4,23–25].

Based on the idea that microwave irradiation heats polar and ionic substances quickly and efficiently, we herein report the attempt to separate ILs from ILs/water mixture by microwave

Abbreviations: [Emim]$^+$, 1-ethyl-3-methylimidazolium; [Bmim]$^+$, 1-butyl-3-methylimidazolium; [BF_4]$^-$, tetrafluoroborate; [TfO]$^-$, trifluoromethanesulfonate; [MS]$^-$, methylsulfate; [PF_6]$^-$, hexafluorophosphate; [Tf_2N]$^-$, bis(trifluoromethylsulfonyl)imide.

* Corresponding author at: Department of Biological Engineering, Inha University, 253 Yonghyung-Dong, Nam-ku, Incheon 402-751, South Korea.
Tel.: +82 32 860 7513; fax: +82 32 872 4046.
E-mail address: ymkoo@inha.ac.kr (Y.-M. Koo).

0021-9673/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.chroma.2010.10.028

heating. Due to their broad application spectrum, separation of hydrophilic ILs ([Bmim][BF_4], [Bmim][TfO] and [Emim][MS]) and hydrophobic ILs ([Bmim][PF_6] and [Bmim][Tf_2N]) from the aqueous ILs solution was studied under microwave irradiation.

2. Materials and methods

2.1. Materials

All ILs were purchased from C-Tri Company (Suwon, Korea) and had a residual chloride content of less than 30 ppm. ILs were dried under vacuum at 60 °C for 24 h before use. All other chemicals used in this work were of analytical grade and used without further purification.

2.2. Microwave-assisted separation

A monomode microwave system (CEM discover, USA) was used for a microwave-assisted separation of ILs from ILs/water mixture. In this microwave system, a continuous well-defined standing wave is generated and irradiation is focused onto the sample which gives homogenous distribution in energy. In addition, the temperature can be precisely controlled and measured by IR sensor.

Experiments were carried out with 1 mL of 50% (w/w) hydrophilic ILs/water mixture or water-saturated hydrophobic ILs in a 10 mL Pyrex reaction vessel. For conventional distillation, IL/water mixture was placed in a vacuum oven at vacuum pressure of 90 kPa and oven temperature of 363.15 K. Microwave-assisted separation was operated in CEM discover system at constant microwave power of 10 W.

2.3. Analysis

Water content in ILs was measured by Karl Fischer titration (831 KF coulometer, Metrohm, Switzerland) using HYDRANAL-Coulomat AG-H reagent. The structures of ILs before and after microwave irradiation were determined by 400 MHz FT-NMR spectrometer (Varian Inova 400, USA) in acetone-D6. Energy consumption of equipments was measured by a digital electricity meter (Inspector II, X-4 Life, Germany).

3. Results and discussion

3.1. Heating behavior of aqueous ILs solution

For hydrophilic ILs such as [Bmim][BF_4], [Bmim][TfO] and [Emim][MS], 50% (w/w) mixture of hydrophilic ILs and water (where ILs are fully miscible with water after vigorously shaking) was used to make a homogeneous mixture. For hydrophobic ILs such as [Bmim][Tf_2N] and [Bmim][PF_6], on the other hand, water-saturated hydrophobic ILs are used since solubilities of water in [Bmim][Tf_2N] and [Bmim][PF_6] were 1.75 and 2.70 wt% at 298.15 K, respectively. As a comparison, temperature history of pure water (in the absence of ILs) at the same power is also shown. As a preliminary experiment, the relationship between microwave power and recovery time was investigated (Table 1). As can be expected from operational point of view, the increase in microwave power could give rise to a dramatic decrease in recovery time, but eruption of aqueous ILs solution (1 mL) from reaction vial (10 mL) occurred beyond 10 W (data not shown). Accordingly, constant microwave power of 10 W was used as the optimal power input throughout the experiments.

Fig. 1 shows heating curves of homogeneous mixtures of ILs and water under microwave irradiation at constant power of 10 W.

Table 1
Effect of microwave power on ILs recovery time from ILs/water mixture by microwave-assisted separation.[a]

Microwave power (W)	Time (min)	Water content (wt%)	Final temperature (°C)
5	15	0.44	122
10	10	0.45	128
15	3.45	0.44	200

[a] Experiments were carried out with 1 mL of 50% [Bmim][BF_4]/water mixture.

Regardless of types of ILs, aqueous ILs solutions could be quickly heated to high temperature under microwave irradiation. Although the polarity of ILs referred by dielectric constant (ε) is far lower than that of water (thus ILs are considered as moderate polar solvents whose ε were in the range of 10–12 compared to 78.4 of water at 298.15 K) [26], their ionic structural properties could make aqueous ILs solution to be heated up much faster than pure water by microwave irradiation. Moreover, the existence of ILs enables aqueous ILs solution to be heated to a temperature exceeding the boiling temperature of pure water at atmospheric pressure by microwave. This phenomenon was also observed by Leadbeater and Torenius, in which ILs were classified as heating aid materials for non-polar solvent under microwave irradiation [23,24].

3.2. Microwave-assisted distillation of aqueous ILs solution

As a result, water in homogeneous mixture of ILs and water was rapidly evaporated by microwave irradiation and ILs containing less than 0.5 wt% water content were obtained as shown in Fig. 2(a). For hydrophilic ILs such as [Bmim][BF_4], [Bmim][TfO] and [Emim][MS], less than 0.5 wt% water content in ILs could be obtained in 6 min from the mixture of ILs and water (1:1, w/w) under microwave irradiation at constant power of 10 W while it took at least 240 min to obtain ILs containing less than 0.5 wt% water content in conventional vacuum oven at 363.15 K with 90 kPa of vacuum pressure (Fig. 2(b)).

Water in hydrophobic ILs could also be effectively removed to a certain extent by microwave irradiation, but different behaviors were observed. Unlike the mixture of hydrophilic ILs and water, water contents in water-saturated [Bmim][Tf_2N] and [Bmim][PF_6]

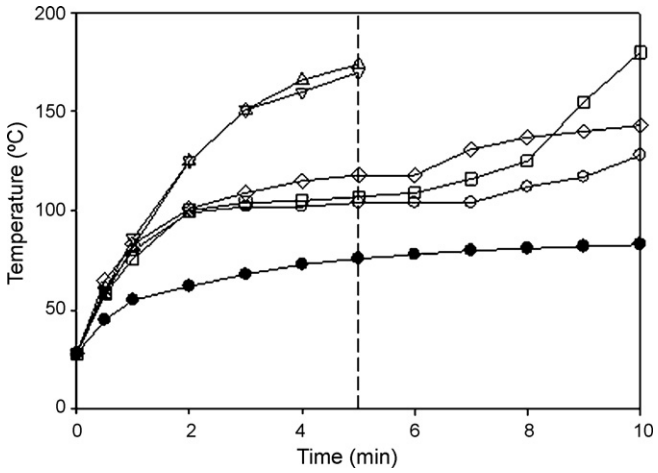

Fig. 1. Temperature changes of aqueous ILs solutions during microwave irradiation. (●): water, (○): [Bmim][BF_4], (□): [Bmim][TfO], (◊): [Emim][MS], (△): [Bmim][Tf_2N], (▽): [Bmim][PF_6]. Experiments were carried out with 1 mL of 50% (w/w) hydrophilic ILs/water mixture or water-saturated hydrophobic ILs. Microwave-assisted separation was performed in CEM discover system (CEM, USA) at constant microwave power of 10 W. Water content was determined by Karl Fischer titration (831 KF coulometer, Metrohm, Switzerland).

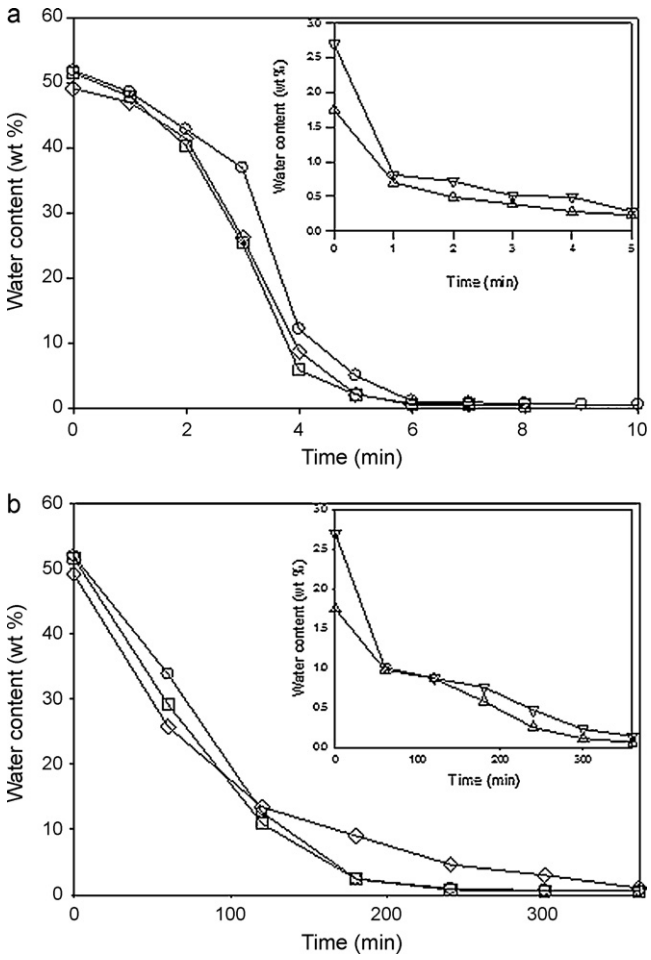

Fig. 2. (a) Water content changes in ILs/water mixtures during microwave-assisted separation; (b) Water content changes in ILs/water mixtures by conventional vacuum oven. Inner graphs in (a) and (b) are water content changes in water-saturated hydrophobic ILs by microwave-assisted separation and conventional vacuum oven, respectively. (◯): [Bmim][BF_4], (□): [Bmim][TfO], (◊): [Emim][MS], (△): [Bmim][Tf_2N], (▽): [Bmim][PF_6]. Experimental conditions for the microwave-assisted separation were same as those in Fig. 1. Conventional vacuum oven was operated at vacuum pressure of 90 kPa with 363.15 K. Water content was determined by Karl Fischer titration (831 KF coulometer, Metrohm, Switzerland) using HYDRANAL-Coulomat AG-H reagent.

were rapidly decreased from 1.75 and 2.70 wt% at 298.15 K to 0.70 and 0.81 wt% in 1 min, respectively, by microwave irradiation, then decreased slowly to 0.23 and 0.28 wt% in 5 min. However, much shorter time is required by microwave irradiation compared with 240 and 300 min in conventional vacuum oven, respectively, to reach similar water contents. During microwave-assisted distillation of aqueous ILs solution, the mixture was heated to as high as 453.15 K as shown in Fig. 1, but the decomposition of ILs would not occur since this temperature is far lower than thermal decomposition temperatures of most of imidazolium-based ILs (676.15 K, 713.15 K, 712.15 K and 622.15 K for [Bmim][BF_4], [Emim][TfO], [Bmim][Tf_2N], [Bmim][PF_6], respectively) [27]. It was well known that microwave energy can efficiently heat up materials in much shorter time but does not have enough energy to break down any chemical bonds [20,21]. No changes in the structure of ILs before and after microwave irradiation were observed in NMR spectra (^1H and ^{13}C NMR spectra not shown), indicating that decomposition of ILs does not occur. Further evaporation of hydrophobic ILs by microwave irradiation resulting in higher temperature will yield much purer ILs, but the decomposition of ILs under these conditions cannot be ruled out at elevated temperatures.

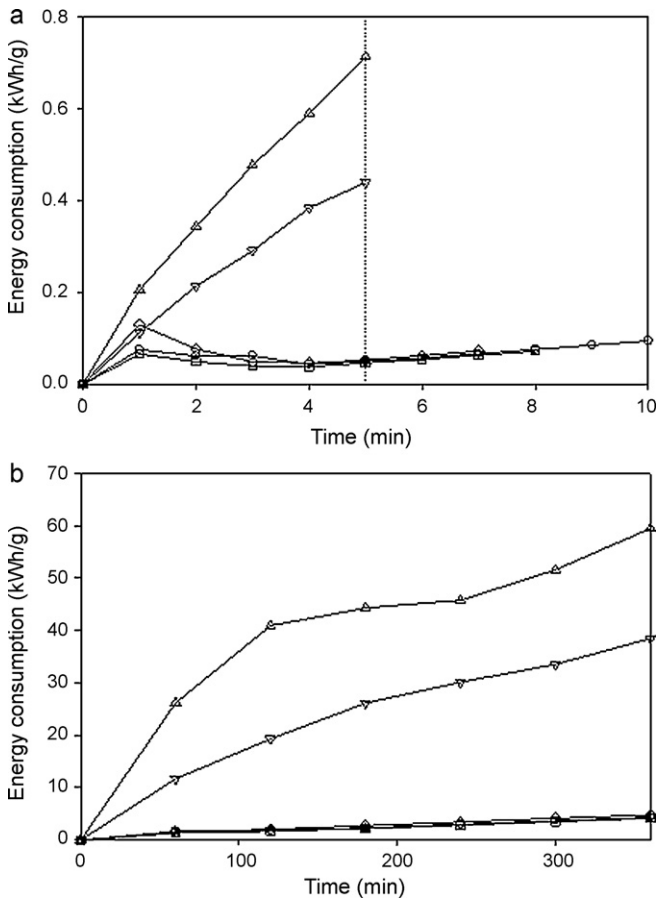

Fig. 3. Accumulated energy consumption per gram distilled water of microwave-assisted distillation (a) and conventional vacuum oven (b). (◯): [Bmim][BF_4], (□): [Bmim][TfO], (◊): [Emim][MS], (△): [Bmim][Tf_2N], (▽): [Bmim][PF_6]. Experimental conditions were same as those in Fig. 2. Energy consumption was measured by a digital electricity meter (Inspector II, X-4 Life, Germany).

3.3. Energy consumption

Microwave irradiation not only significantly reduces time required to separate ILs from ILs/water mixture but also lowers energy consumption. As can be clearly seen in Fig. 3, accumulated energy consumption per gram of evaporated water by microwave irradiation was far lower than that consumed in conventional vacuum oven if we assume that all input energy is consumed to heat the mixture of ILs and water.

For example, energy consumptions per gram of evaporated water from the homogeneous mixture of hydrophilic ILs and water (1:1, w/w) by microwave-assisted separation were at least 52 times more efficient than those in conventional vacuum oven. It can be explained by direct heating of aqueous ILs solution by microwave irradiation instead of heat transfer from the reaction container as in conventional methods. Direct heating improves energy transfer and thus reduces the amount of energy used for heating. In addition, energy required to distill water from water-saturated hydrophobic ILs was much higher than that from water containing hydrophilic ILs in both recovery methods although water content in hydrophilic ILs is much higher compared to hydrophobic ILs.

4. Conclusions

In this study, it has been demonstrated that microwave irradiation can be as a good tool for the separation of ILs from the mixture of ILs and polar solvent, specifically, from ILs/water mixture. This

is also true for the mixture of ILs with non-polar volatile solvents. Microwave-assisted distillation will be more effective in a much diluted ILs mixture resulted from various applications including dissolution and regeneration of cellulosic material, where time and energy-saving method is required for the recovery of ILs from such diluted solution. Practically, microwave-assisted separation could be used to recover ILs efficiently in sense of time and energy as well as relevant purity.

Acknowledgements

This work was financially supported by the Ministry of Knowledge Economy, Korea through the Cleaner Production Technology Development Project. The authors are grateful to Kenneth R. Seddon (QUILL, UK) for his helpful discussions.

References

[1] K.R. Seddon, J. Chem. Tech. Biotechnol. 68 (1997) 351.
[2] S.G. Cull, J.D. Holbrey, V. Vargas-Mora, K.R. Seddon, G.J. Lye, Biotechnol. Bioeng. 69 (2000) 227.
[3] M.J. Earle, K.R. Seddon, Pure Appl. Chem. 72 (2000) 1391.
[4] Y. Lu, W. Ma, R. Hu, X. Dai, Y. Pan, J. Chromatogr. A 1208 (2008) 42.
[5] V.I. Parvulescu, C. Hardacre, Chem. Rev. 107 (2007) 2615.
[6] P. Wasserscheid, T. Welton, Ionic Liquid in Synthesis, 2nd ed., Wiley-VCH, Weinheim, 2008.
[7] F. van Rantwijk, R.A. Sheldon, Chem. Rev. 107 (2007) 2757.
[8] S.H. Ha, M.N. Lan, S.H. Lee, S.M. Hwang, Y.-M. Koo, Enzym. Microb. Tech. 41 (2008) 480.
[9] S.H. Ha, N.M. Hiep, S.H. Lee, Y.-M. Koo, Bioprocess Biosyst. Eng. 33 (2010) 63.
[10] H. Zhao, S. Xia, P. Ma, J. Chem. Tech. Biotechnol. 80 (2005) 1089.
[11] S.H. Ha, R.N. Menchavez, Y.-M. Koo, Korean J. Chem. Eng. 27 (2010) 1360.
[12] R.P. Swatloski, S.K. Spear, J.D. Holbrey, R.D. Rogers, J. Am. Chem. Soc. 124 (2002) 4975.
[13] S.H. Ha, N.L. Mai, G. An, Y.-M. Koo, Bioresour. Technol. (2010), doi:10.1016/j.biortech.2010.07.108.
[14] H. Zhao, Chem. Eng. Commun. 193 (2006) 1660.
[15] S.H. Ha, M.N. Lan, Y.-M. Koo, Enzym. Microb. Tech. 47 (2010) 6.
[16] S. Hayashi, H. Hamaguchi, Chem. Lett. 33 (2004) 1590.
[17] S.H. Lee, S.H. Ha, C.-Y. You, Y.-M. Koo, Korean J. Chem. Eng. 24 (2007) 436.
[18] P. Lindström, J. Tierney, B. Wathey, J. Westman, Tetrahedron 57 (2001) 9225.
[19] R.S. Varma, Green Chem. 1 (1999) 43.
[20] A. Loypy, Microwaves in Organic Synthesis, Wiley-VCH, Weinheim, 2002.
[21] C.O. Kappe, D. Dallinger, S.S. Murphree, Practical Microwave Synthesis for Organic Chemists: Strategies, Instruments and Protocols, Wiley-VCH, Weinheim, 2009.
[22] J. Hoffmann, M. Nüchter, B. Ondruschka, P. Wasserscheid, Green Chem. 5 (2003) 296.
[23] N.E. Leadbeater, H.M. Torenius, J. Org. Chem. 67 (2002) 3145.
[24] N.E. Leadbeater, H.M. Torenius, H. Tye, Comb. Chem. High Throughput Screen 7 (2004) 511.
[25] F.Y. Du, X.H. Xiao, G.K. Li, J. Chromatogr. A 1140 (2007) 56.
[26] H. Weingärtner, Z. Phys. Chem. 220 (2006) 1395.
[27] J.G. Huddleston, A.E. Visser, W.M. Reichet, H.D. Willauer, G.A. Broker, R.D. Rogers, Green Chem. 3 (2001) 156.