Desalination and Water Treatment
www.deswater.com

34 (2011) 326–329
October

doi: 10/5004/dwt.2011.2884

Concentration of ionic liquids from aqueous ionic liquids solution using electrodialyzer

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Received 3 September 2010; Accepted 3 January 2011

ABSTRACT

Ionic liquids (ILs) have great potential for industrial use as green alternative solvents. However, the high price of ILs restricts their applications. Since ILs are easily lost in its application process, it is necessary to seek for an effective approach to recover and concentrate ILs from ILs/water mixtures. In this paper, an electrodialysis (ED) process was proposed to concentrate the model ionic liquids of 1-butyl-3-methylimidazolium chloride ([BMIM]Cl). It was demonstrated that ILs could be successfully concentrated from aqueous ILs solution using the permselectivity of ion exchanges membranes under DC electric field. The structure of the products was identified with ^{1}H NMR. The effects of applied voltage and flow rate were intensively investigated. The experimental results showed that the increase in applied voltage and the decrease in flow rate would lead to the better performance of ED cell.

Keywords: Ionic liquids; Electrodialysis; Concentration; Voltage; Flow rate; Energy consumption

1. Introduction

Room temperature ionic liquids (ILs) are composed of ions comprising a relatively large asymmetric organic cation and an inorganic or organic anion. In recent years, the synthesis and application of ILs have received considerable interest due to their potential or demonstrated applications such as synthetic chemistry, catalysis, separation technologies, bio-enzymatic reactions [1–4]. For example, the dissolution of cellulose using ionic liquids has been providing a new platform for ‘‘green’’ cellulose utilization. Cellulose can be dissolved, without derivation, in some hydrophilic ionic liquids, such as 1-butyl-3-methylimidazolium chloride (BMIMCl) and 1-allyl-3-methylimidazolium chloride (AMIMCl). However, ILs are often lost in these processes. Furthermore, many of the current ILs are expensive to produce and/or difficult to dispose of [5]. Therefore, it is desirable to seek an effective approach to recover and concentrate ionic liquids from ionic liquids/water mixtures. Various methods, such as evaporation, ionic exchange, pervaporation, reverse osmosis and salting out are used to recover the ionic liquids [6]. These processes often require high energy consumption.

Electrodialysis (ED) is a membrane separation process based on the selective migration of aqueous ions through ion-exchange membranes as a result of an electrical driving force [7,8]. This technique represents one of the most important methods for desalting solutions. In this study, it was thought that the ion liquids could possibly be concentrated by using electrodialyzer as the cations and anions of ILs have their own charges. For that purpose, [BMIM]Cl was used as a model ionic liquid. A schematic diagram, which simply describes the principles of the concentration of ILs using electrdialyzer, is shown in Fig. 1. As shown in Fig. 1, the feed solutions of [BMIM]Cl was added to dilute chamber. Two electrodes are positioned, one on either side parallel to the membranes. Applying a voltage to the electrodes generates an electric field. It is well known that

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Presented at the AMS6/IMSTEC10, The 6th conference of the Aseanian Membrane Society in conjunction with the 7th International Membrane Science and Technology Conference, Sydney Australia, November 22–26, 2010

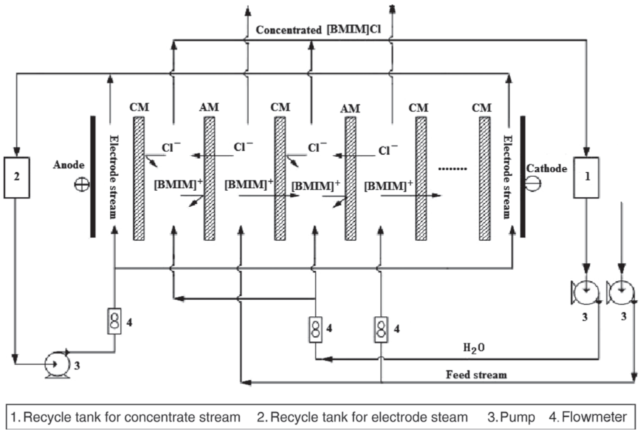

Fig. 1. Schematic illustration of the concentration of ionic liquids from aqueous ionic liquids solution using electrodialyzer.

the anion-exchange membrane permits the passage of anions only while the cation-exchange membrane permits the passage of cations only. Therefore, Cl^- migrated through the anion exchange membranes while $[BMIM]^+$ ions passed through the cation-exchange membranes under the action of DC electric field. Both $[BMIM]^+$ and Cl^- ions entered into concentrated chamber. Thus, the concentrated ILs of [BMIM]Cl could be obtained in the concentration chamber.

In this study, the effects of applied voltage and flow rate were intensively investigated. The structure of the products was identified with ^1H NMR. The yield ratio and purity of the products were determined by HPLC. To our best knowledge, it is the first example to recover and concentrate the ILs from ILs/water mixture using ED.

2. Experimental

2.1. ED set-up and materials

The experimental ED set-up is comprised of a circulation system, a DC power supply unit, ion exchange membranes and spacer. The dimensional sizes of the self-made electrodialyzer are 300 mm × 120 mm. The electrodialyer has 8 stacks. The thickness of each compartment is 2.0 mm. In ED cell, two titanium plated with ruthenium electrodes are positioned, one on either side parallel to the membrane. Three tanks are used for holding dilute solution, concentrated solution and electrode solution. Commercial cation- and anion-exchange membranes, JCM-10 (CEM) and JAM-l0 (AEM), were supplied by Beijing Huan Yu Li Da Equipment Ltd Co. Table 1 shows the properties of JCM-10 and JAM-l0 membranes. The cation- and anion-exchange membranes were alternately arranged in the electrodialyzer.

In our laboratory, [BMIM]Cl was synthesized by the reaction of 1-methylimidazole and 1-chlorobutane under argon atmosphere. The synthesis was conducted with magnetic agitation condition at 70°C for 48 h. After the reaction was completed, the product and unreacted starting materials were separated in two liquid phases. The products were washed with ethylacetate for four times. Rotary vacuum evaporation was used for the complete removal of unreacted materials and washing liquid. Na_2SO_4 solution with a conductivity of around 5000 mg/l was used as electrode solution. [BMIM]Cl solution was continuously added into the dilute chamber by maintaining the [BMIM]Cl concentration of 100 g l^{-1}. The solutions in the electrode chamber and concentrated chamber were circulated in a closed system, respectively. After operation for 10 min, the electrodialyzer was turned off. The concentrations of the $[BMIM]^+$ and Cl^- in the concentrated chamber was measured.

Table 1
Properties of JCM–10 and JAM-l0 membranes

Kind of ion exchange membrane	Homogeneous ion exchange memberame	
	JCM–10	JAM-10
Degree of crosslinking	10	10
Thickness (mm)	0.11–0.13	0.11–0.12
Water content (%)	≥24	≥20
Exchange capacity meq/g (dry)	≥1.8	≥1.4
Transport number (%)	≥95	≥88
Bursting strength (Mpa)	≥0.15	≥0.15

2.2. Analytical methods

The concentrations of $[BMIM]^+$ was detected using High Performance Liquid Chromatography (SCL-10Avp, Shimadzu). Agilent Zorbax 300-SCX (4.6 mm × 150 mm, 5 μm) was used. The mobile phase was the mixture of methanol and KH_2PO_4 at the ratio of 3:7. The mobile phase flow was 1.0 ml/min. The detection wave length was 212 nm. Injection volume was 60 μl. Nuclear magnetic resonance spectroscopy was performed (AVANCE+400, BRUKER) to further confirm the structure of the products.

3. Results and discussion

3.1. Effect of voltage

As the applied voltage has great influence on the ED efficiency, concentration experiments were conducted at four applied voltages; 6,8,10 and 12 V. Fig. 2 shows the profiles of [BMIM]Cl concentration in the concentrate chamber with applied voltage. As shown in Fig. 2, [BMIM]Cl could be concentrated much more rapidly

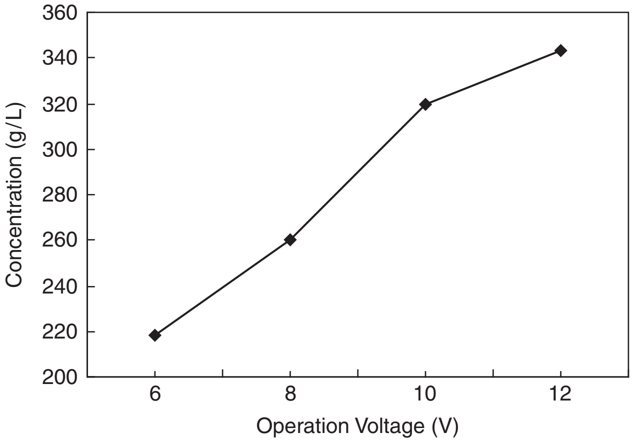

Fig. 2. Variations of ILs concentration in the concentrate chamber with applied voltages.

with the increase in the applied voltage. For example, under the voltage of 12 V, the [BMIM]Cl could be enriched from 100 gl^{-1} to 343 gl^{-1} after 10 min operation. In contrast, the [BMIM]Cl concentration in the concentrate chamber was only 218 gl^{-1} in the case of 6 V voltage. It was expected that the concentration process could be completed within a short time so as not to loss too much [BMIM]Cl. Therefore, a relatively high applied voltage was required. However, too high applied voltage is associated with high energy consumption. Moreover, high applied voltage would possibly result in serious membrane fouling and concentration polarization. In view of the above fact, 12 V was selected for the subsequent experiments.

3.2. Effect of flow rate

Fig. 3 shows the variation of [BMIM]Cl concentration in the concentrate chamber with the flow rate. It was noted from the figure that the [BMIM]Cl concentration in the concentrate chamber obtained at three different flow rate of 40 lh^{-1}, 60 lh^{-1} and 80 lh^{-1} varied within a narrow band. Moreover, the product losses associated with 60 lh^{-1} and 80 lh^{-1} are almost the same as that at 40 lh^{-1}(Fig. 4). This would suggest that the influence of flow rate on the concentration and product loss is negligible. Although increasing flow rate decreases concentration polarization due to residence time reduction, the high flow rate usually requires high energy. Therefore, a medium flow rate of 60 lh^{-1} is recommended in our study.

3.3. Analyses of energy consumption

The energy consumption required for treating 1 l of [BMIM]Cl is defined in the following equation:

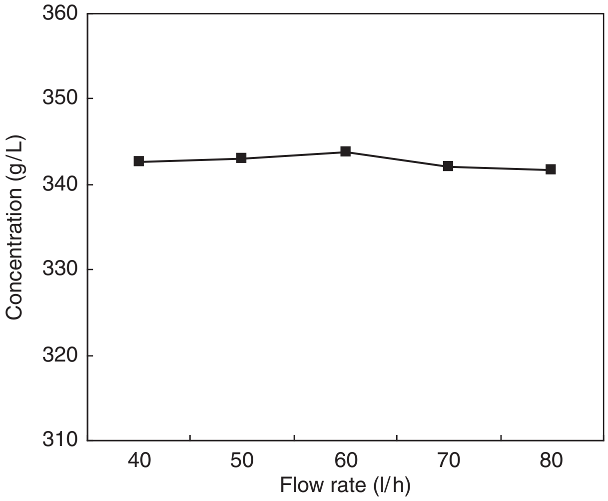

Fig. 3. Variations of ILs concentration in the concentrate chamber with flow rates.

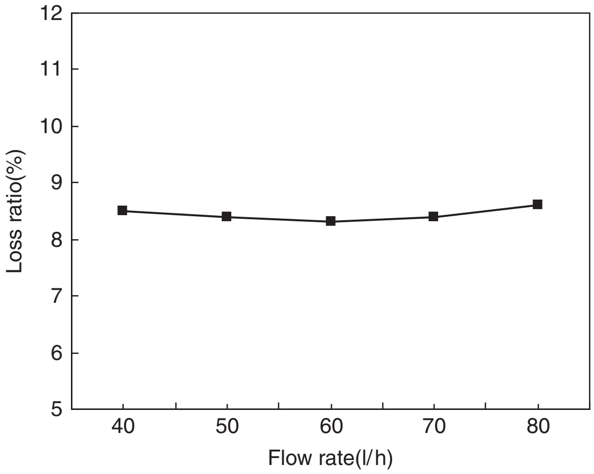

Fig. 4. Variations of ILs loss rate with flow rates.

$$P = \frac{\int_0^t EIdt}{V_{do}} \tag{1}$$

where E is the applied voltage, I is the electric current, t is the operation time, and V_{do} is the initial volume of feed solution. When the flow rate in the dilute compartment are kept at 60 lh-1, the variation of the energy consumption with applied voltage is shown in Fig. 5. It was noted that both overall and membrane stack energy consumptions have emerged as increasing trend with the increase in the applied voltages. Under the selected voltage of 10 V, the energy consumption was 0.35 W·h.–l.

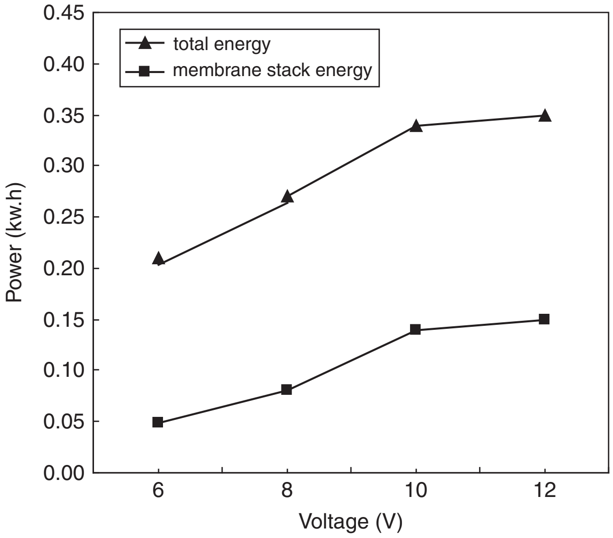

Fig. 5. Variations of energy consumption with applied voltages.

3.4. Recovery of ED-concentrated [BMIM]Cl

As the above-mentioned, the appropriate operation conditions of ED were selected as: the applied voltage, 12 V; and the flow rate, 60 lh^{-1}. Under the given conditions, the concentration of [BMIM]Cl could reach 343 gl^{-1} after ED process. In order to further reuse the ED-concentrated [BMIM]Cl, the water contained in the ED concentrated [BMIM]Cl was then vaporized by vacuum distillation. After drying at 70~80°C for 8~24 h, the transparent [BMIM]Cl was finally obtained. The structure of the product was further identified by ^{1}H NMR (Brucker AV400MHz, Germany). The resulting data are as follows:

[BMIM]Cl: 8.69(s, 1H), 7.46(m, 1H), 7.41(m, 1H), 4.18(s, 2H), 3.88(s, 3H), 1.84(m, 2H), 1.30(m, 2H), 0.91(t, 3H)

As we expected, no anomaly peak occurred in the ^{1}H NMR spectra. These signals further confirmed that the [BMIM]Cl with high purity was successfully recovered. The purity of IL was over 98% based on the HPLC results. It should be point out that the combination of ED and vacuum distillation save much more energy in comparison with that using single vacuum distillation. It was calculated that 9 kg steam energy consumption for the recovery of 1.0 kg [BMIM] Cl ionic liquids was required using the direct distillation. As a comparison, the total energy consumption is only 1.92 kg steam after combining ED and distillation. It was calculated that about 78% energy was saved using the proposed process.

4. Conclusions

To the authors' best knowledge, this is the first work to concentrate and recover ionic liquid using ED process. The effects of applied voltage and flow rate on ED performance were investigated. The appropriate operation conditions for the present unit were selected as: the applied voltage, 12 V; and the flow rate, 60 lh^{-1}. Under the given conditions, the concentration of [BMIM]Cl could reach 343 gl^{-1} after ED process. Energy consumption was also analyzed under different conditions. Further studies were conducted to understand the feasibility of the recovery of [BMIM]Cl using a combination process of ED and vacuum distillation. It was found that the combination reduce the energy penalty of evaporating all of the water.

Acknowledgements

The project was supported by National Natural Science Foundation of China (20606001 and 20776015) and Beijing Nova Programme(2007A020).

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