Synthesis and characterization of ionic liquid polymer composite with zeolite and its application for carbon dioxide capture

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Abstract. Among the different ways to capture carbon dioxide (CO_2), ionic liquid technology is one of the prominent approaches and gained the interest of researchers to improve this technology from time to time. In this study, we have prepared and characterized a novel ionic liquid polymer composite with zeolite and tested its efficiency to capture CO_2. The ionic liquid monomer, 1-vinyl-3-ethylimidazolium bis(trifluoromethylsulfonyl)imide [Veim][Tf2N] was polymerized through free radial polymerization process adding zeolite to form poly[Veim][Tf2N] zeolite polymer composite. The synthesized polymer ionic liquid zeolite composite was characterized by FT-IR, FE-SEM and EDX. The formation of polymer ionic liquid zeolite composite was indicated by the presence of zeolite peaks in FT-IR spectra. Additionally, the EDX results were confirmed the presence of zeolite in the prepared composite. Finally, to prove the efficiency of prepared polymer ionic liquid zeolite composite, the adsorption studies have been conducted using CO_2 adsorption cell. The results revealed the capability of ionic liquid zeolite polymer composite in adsorbing high amount of CO_2 and recorded the highest pressure drop compared to other polymer ionic liquid and monomer ionic liquid materials.

1. Introduction

In recent years, the development of industrial revolution has created higher demand for energy that is being supplied by thermal power plants. The higher production of energy to meet the demand of industrial needs is primarily achieved by the combustion of fossil fuels (i.e., coal, oil and gas), whose combustion creates a negative impact on the environment and producing excess of greenhouse gases that are mainly consist of carbon dioxide (CO_2). According to United States Environmental Protection Agency (2015), CO_2 is contributing for the largest percentage of greenhouse emissions, which is roughly 82% from 6587 million metric tons in 2015 compared to other greenhouse gases [1].

NOAA's Earth System Research Laboratory and Scripps Institution of Oceanography (May 2016) were responsible to measure the emission of greenhouse gases in the atmosphere, and both the agencies have reported that concentration of CO_2 in the atmosphere has increased by more than 2.0 ppm every year from 2012 to 2015. They were also reported that, the estimated average amount of CO_2 in 2016 (404.16 ppm) was increased by almost 4.0 ppm when compared with the reported value of average amount of CO_2 in 2015 (400.30 ppm) [2].

The above data clearly indicates that, the concentration of CO_2 in the atmosphere is increasing every year. Therefore, many researchers and scientists have paid attention to discover the new technologies and methods that control the concentration levels of CO_2 in the atmosphere, which is the prime contributor of greenhouse gases. Several methods have been discovered to capture and separate CO_2 physically and chemically including sorption processes and membrane separations [3]. In recent years, ionic liquids have been proposed as promising alternatives to the conventional volatile solvents, which possess high CO_2 solubility. Basically, ionic liquids are low melting point salts with negligible vapour pressure, thermal stability with high CO_2 solubility. The trivial negative impact of ionic liquids to the environment has created the advantage and opportunity for their use in the CO_2 capture [4].

The major advantage of ionic liquids is their excellent solvation property for a variety of organic and inorganic compounds and their ability to undergo modification according to specific objectives and requirements with the marginal effect to environment is sufficient for them to be known as 'greener solvents' [5, 6]. Even though, ionic liquids have the advantage for the absorption of CO_2, the higher practical Henry's Law constant of ionic liquids does not help in the effective application of ionic liquids. Additionally, the liquid structure of ionic liquids has lower thermal stability and makes the process of CO_2 separation difficult to be done. Therefore, researchers were attempted to find the new ways to enhance the efficiency of CO_2 sorption performance by polymerization of ionic liquids [7]. Ionic liquid polymers were found to have higher sorption capacities than the room temperature ionic liquids. For instance, a study reported that the performance of poly(ionic liquid)s i.e., P[VBTMA][BF4] and P[MATMA][BF4] was increased over 7.6 capacities with 6.0 times of the efficiency compared to their monomer [bmim][BF4] [8]. Additionally, a large variety of adsorbents have been incorporated with ionic liquids to improve the CO_2 adsorption including activated carbon, zeolite, metal organic framework (MOF), alkali metal carbonate and amine based solids [9].

Therefore, in the present study, zeolite has been considered as the adsorbent/solid phase because of its abundant quantity on the earth and its low cost gives the advantage for the process to become more economical similar to activated carbon [10]. Additionally, zeolite has the crystalline molecular structure of aluminium and silicon atoms surrounded by four oxygen atoms, or it can be aluminosilicate consists of uniform porous surface enable the undesired molecule to be adsorbed by penetrating it. Therefore, it is proposed that the incorporation of zeolite into ionic liquid polymer may enhance the adsorption capacity of polymer ionic liquid [11-13]. Hence, the objective of this study is to synthesize and characterize the polymer ionic liquid zeolite composite and to investigate the efficiency of prepared ionic liquid zeolite polymer composite for the sorption of CO_2. The results of this study were also composed with the existed literature to prove the efficiency of synthesized ionic liquid zeolite polymer composite.

2. Experimental

2.1. Materials
The chemicals used to synthesize the ionic liquids including ethanol, bromoethane and ethyl acetate were obtained from Merck, New Jersey, USA. Lithium bis(trifluoromethylsulfonyl)imide, 1-vinylimidazole, zeolite 13X, trimethylolpropane trimetacrylate were purchased from Sigma-Aldrich, St. Louis, Missouri, USA. The chemicals used as supplied without further purification. Appropriate amount (about 1.0%) of salts were dissolved in ethanol to prepare ionic liquid zeolite polymer composite.

2.2. Synthesis of ionic liquid monomers

Bromoethane and 1-vinylimidazole were used as primary materials for the synthesis of 1-vinyl-3-ethylimidazolium bromide [Veim][Br] ionic liquid. For this, 33 g of 0.3 mol bromoethane was added to 28 g of 0.3 mol 1-vinylimidazole under the vigorous stirring in ice bath. Then, the solution was heated to 40 °C for 2.0 hrs to ensure the reaction of total component. Thereafter, the sample was dried in rotary evaporator for 5.0 hrs at 70 °C and drops the pressure until 50 mmHg to ensure that the prepared ionic liquid was completely dry.

For the preparation of second ionic liquid monomer i.e., 1-vinyl-3-ethylimidazolium bis(trifluoromethylsulfonyl)imide [Veim][Tf2N], ionic liquid [Veim][Br] and Li[Tf2N] were used as starting materials. For this, 40 g of 0.197 mol [Veim][Br] was poured and mixed into 20 mL of distilled water. Then, 62 g of 0.216 mol Li[Tf2N] was added to [Veim][Br] in 1:1 (v/v) ratio by drop wise to avoid the excess heat generation. Two phases of liquids were formed on mixing at room temperature under constant stirring, indicating [Veim][Tf2N] formation at bottom phase and aqueous Li[Br] at top phase. The mixture was then separated using a separating funnel and the desired product [Veim][Tf2N] was washed thoroughly with distilled water and the process was repeated few times to ensure that there is no Br- remained. Distilled water containing Br- was removed using separating funnel and using rotary evaporator to ensure the removal of water completely.

2.3. Synthesis of ionic liquid polymer composite zeolite

The ionic liquid polymer, 1-vinyl-3-ethylimidazolium bis(trifluoromethylsulfonyl)imide was prepared by conventional free-radical polymerization. Initially, 6.0 g of 0.015 mol ionic liquid monomer i.e., [Veim][Tf2N] was added to 6.0 g of 0.13 mol ethanol and then the solution was purged with nitrogen and stirred well at 300 rpm for 30 minutes. Next, 120 mg of 0.72 mmol 2,2'-azobis isobutyronitrile (AIBN) and 300 mg of 0.9 mmol trimethylolpropane trimetacrylate (TRIM) were added to the above solution and purged again with nitrogen for another 10 minutes. Thereafter, the mixture was heated at 65 °C for 30 minutes without any purging under nitrogen. A white gel-elastic solid was formed at the end of stirring, then it has been diluted with ethanol to remove any unreacted monomer. The solution was poured into distilled water to precipitate the polymer composite. The samples were washed carefully with ethanol for few times prior its filtration using filter funnel and filter paper. After the filtration, the samples were dried using rotary evaporator to remove solvents at 55 °C with minimum pressure of 80 mmHg for 15 minutes. Likewise, the preparation of ionic liquid polymer zeolite composite is similar to the preparation of poly[Veim][Tf2N] except the addition of zeolite 13X along with the ionic liquid monomer as well as ethanol with mass 180 mg with 6.0 g [Veim][Tf2N]. The resulted poly[Veim][Tf2N] composite zeolite was appeared to be white elastic-solid which contain white powder of zeolite, and it is quite transparent elastic-solid compared to poly[Veim][Tf2N] (Fig. 1).

Figure 1. Poly[Veim][Tf2N] zeolite composite

2.4. *Characterization of samples*

The fabricated polymer composite was characterized by fourier transform infrared spectroscopy (FT-IR) (Perkin Elmer Spectrum One) to evaluate the incorporation of zeolite into polymer ionic liquid. Next, the field emission scanning electron microscopy (FE-SEM) with energy dispersive X-ray spectroscopy (EDX) (Zeiss Supra 55 VP) was used to observe the crystalline structure and morphology of the sample, as well as to analyze the elemental composition in the prepared polymer composite. Finally, the ionic liquids were characterized using ^{1}H NMR, ^{13}C NMR (Bruker Avance 500 MHz).

2.5. *Application of samples to CO_2 capture*

Ionic liquid monomer [Veim][Tf2N] and its polymer composite materials have been tested for CO_2 adsorption using CO_2 adsorption cell at room temperature 298 K with the initial pressure exerted at 10 bars. This equipment measured the pressure drop of CO_2 gas after passing through the sample. Amount of CO_2 adsorbed by the samples has been analysed using material balance before and after the test and compressibility factor was calculated using Soave-Redlich-Kwong (SRK) equation of state as shown below.
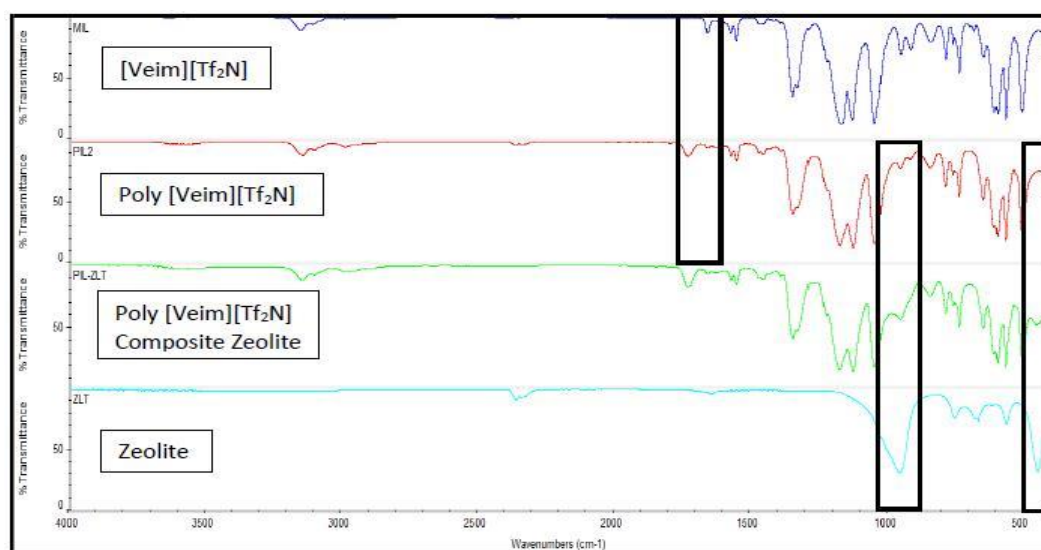
$$P = \frac{RT}{(Vm - b)} - \frac{a}{\sqrt{T}\,Vm(Vm + b)}$$

Where, P is the gas pressure; R is the gas constant; T is temperature; Vm is the molar volume (V/n); a & b are the constants to correct the attractive potential of molecules and volume respectively.
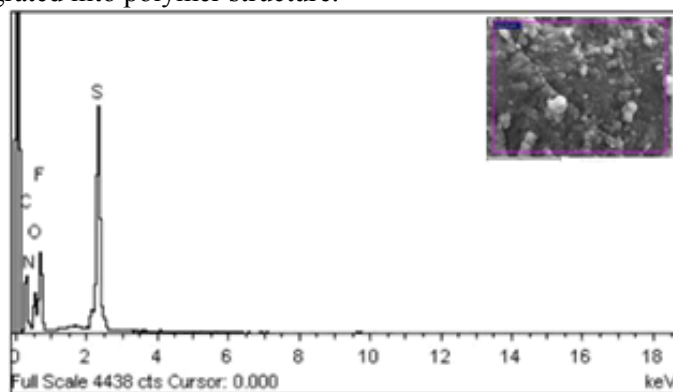
3. Result and discussion

3.1. *Characterization of samples*

The ionic liquid monomers namely [Veim][Br] and [Veim][Tf2N] were characterized using H^1 NMR to verify their purity. Polymeric materials including poly[Veim][Tf2N] and poly[Veim][Tf2N] zeolite composites were characterized by FT-IR and compared the respective peaks of monomer, polymer and zeolite. Fig. 2 exhibited some difference among the peaks of monomer and polymer as the intensity at the range 1600-1680 cm^{-1} is very weak for poly[Veim][Tf2N] and higher for the monomer. Basically, this range indicates the presence of non-aromatic alkenes. Therefore, the results expressed that alkene (C=C) from the monomer was successfully bonded and connected to same ionic liquid molecule to form polymer structure. At the peak 1729 cm^{-1}, its intensity for polymer was higher compared with monomer, which indicates the presence of carbonyl group (C=O) from TRIM. Poly(Veim][Tf2N] zeolite composite was characterized by FT-IR and compared with poly[Veim][Tf2N] ionic liquid. In the same figure, the difference has been displayed in the black box indicating the higher intensity peak at 950-1000 cm^{-1} and the presence of peak at 420-500 cm^{-1} for zeolite polymer composite compared to non-composited polymer. Actually, both the peaks were common for zeolite which represents the tetrahedral characteristic of the internal QO4 where Q is Si or Al [14]. Based on this different, it is confirmed that zeolite is completely incorporated into polymer and resulted to form a composite.
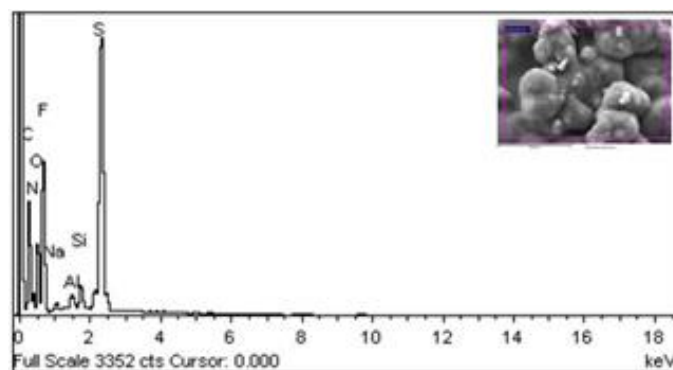
Figure 2. FTIR spectra of [Veim][Tf$_2$N], poly[Veim][Tf$_2$N], poly[Veim][Tf$_2$N] zeolite composite and zeolite.

Additionally, the polymer composite material was characterized by Energy Dispersive X-ray (EDX) and represented in Fig. 3 and Fig. 4. The EDX analysis showed that the major elements in both the polymers were carbon, oxygen, fluorine and sulphur. Hence, based on Fig. 4, it is revealed that the presence of zeolite components such as aluminium and silicon in the polymer indicates that the zeolite was successfully integrated into polymer structure.
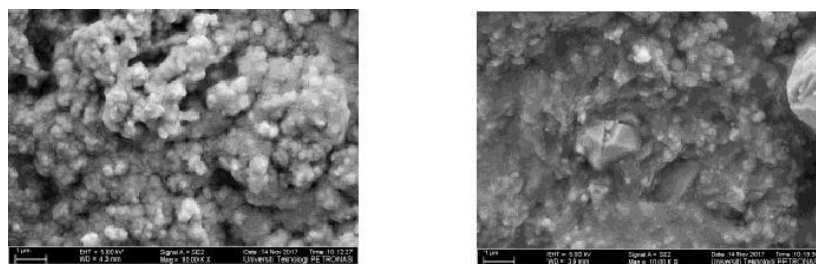

Figure 3. EDX analysis for Poly [Veim][Tf2N]

Figure 4. EDX analysis of Poly[Veim][Tf2N] zeolite composite

Besides, the surface morphology of the polymeric materials was determined using field emission scanning electron microscopy to observe the porosity and structure of polymers. Figure 5 indicates that the porosity of polymer was reduced after zeolite introduction into the polymer structure. Even though there is reduction in the porous structure, it indicates that zeolite if fully mixed with the polymer and the structure of zeolite itself is microporous which would increase the efficiency of CO_2 adsorption process.

Figure 5. FESEM morphology at magnification 10000;
Left: Poly[Veim][Tf2N], Right: Poly[Veim][Tf2N] zeolite composite
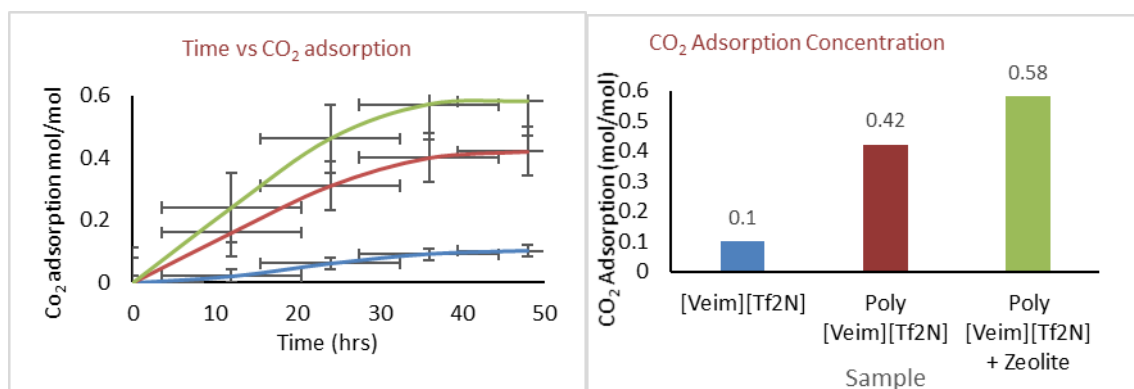
3.2. Application of samples for CO_2 Capture
A CO_2 adsorption cell was used to evaluate the capability of prepared polymer composite samples for CO_2 capture. This equipment measured the equilibrium pressure of CO_2 after passing through the sample. The same initial pressure was exerted for all the samples i.e., 10 bars and the adsorption process was conducted for about 48 hrs at ambient temperature. The value of pressure was being recorded for every 60 sec. CO_2 concentration has been calculated using material balance before and after the adsorption experiment using the following Peng-Robinson equation of state.

$$CO_2 \text{ uptake} = n = \frac{P_{ini} \cdot V_{tot}}{Z_{ini} \cdot R \cdot T_{ini}} - \frac{P_{eq}(V_{tot} - V_{sample})}{Z_{eq} \cdot R \cdot T_{eq}}$$

where n = moles of CO_2 captured; P_{ini} = initial pressure obtained in the absence of sample after expansion of the gas sample from the bomb into the whole system; V_{tot} = total volume of system; Z_{ini} = compressibility factor ($P_{ini} \times T_{ini}$); Z_{eq} = compressibility factor ($P_{eq} \times T_{eq}$); P_{eq} = pressure at equilibrium; V_{sample} = volume of sample; R is the ideal gas constant; T_{ini} = initial temperature and T_{eq} = temperature at equilibrium.

The SRK equation of state has determined the compressibility factor of CO_2, which was found to be 0.894. Based on the results in Fig. 6, it is proved that poly [Veim][Tf2N] zeolite composite is capable to provide higher adsorption capacity compare to the poly [Veim][Tf2N] and [Veim][Tf2N] ionic liquid monomer. Further, the efficiency of the prepared poly[Veim][Tf2N] zeolite was compared with the reported methods, which indicated the clear improvement in CO_2 adsorption when zeolite is incorporated into ionic liquid polymer material [15-17].

Figure 6. CO_2 adsorption for [Veim][Tf2N], poly[Veim][Tf2N],
and poly[Veim][Tf2N] zeolite composite evaluated by CO_2 adsorption cell

4. Conclusion

Ionic liquid polymers namely poly[Veim][Tf2N] and poly[Veim][Tf2N] zeolite composite was successfully synthesized through free radical polymerization process from its monomer [Veim][Tf2N]. During the polymer composite formation 2,2'-azobis(isobutyronitrile) (AIBN) and trimethylolpropane trimethacrylate (TRIM) were added as initiator and cross linker respectively. The synthesized polymer material composites have been characterized using FT-IR, EDX to evaluate the composition of zeolite in the polymer structure. The morphology of the polymer surface was also analysed using FESEM to observe porosity of the polymer. The results showed that zeolite was successfully incorporated into the polymer.

The performance of synthesized ionic liquid materials has been tested using CO_2 adsorption cell to evaluate the adsorption capacity between the polymer material either composited or non-composited and also the ionic liquid monomer. From the results, it is proved that ionic liquid composite polymer gave the best performance as expected by providing higher adsorption capacity compare to non-composited and ionic liquid monomer. The composition of polymer ionic liquid composite i.e., combination between external adsorbent (zeolite) and enhancement of ionic liquid into polymer was believed to influence the efficiency of CO_2 capture. Future work is also recommended to analyse the best desorption process for CO_2 from polymer material to separate CO_2 and to reuse the adsorbent material. Also, proper optimisation between the amount of polymer ionic liquid and external adsorbent is very necessary to increase its efficiency with lower cost.

References
[1]   Shaun A R, Creason J, Jameel A, Sara O, Jeffrey E P and Robert H B 2015 Global mitigation of non-CO_2 greenhouse gases: marginal abatement costs curves and abatement potential through 2030 *J. Integr. Environ. Sci.* **12** 155-168
[2]   Min L, Jiabing W, Zhu X, He H, Jia W and Xiang W 2015 Evolution and variation of atmospheric carbon dioxide concentration over terrestrial ecosystems as derived from eddy covariance measurements *Atmos. Environ.* **114** 75-82
[3]   Roda B, Nancy L, Denis R, Denis R, CécileV and Eric F 2006 Membrane processes for post-combustion carbon dioxide capture: A parametric study *Energy* **31** 2556-2570
[4]   Magaret S, Moniruzzaman M and Masahiro G 2016 Recent advances in exploiting ionic liquids for biomolecules: solubility, stability and applications *Biotechnol. J.* **11** 1000-1013

[5]   Han D and Row K H 2010 Recent applications of ionic liquids in separation technology *Molecules* **15** 2405-2426

[6]   Animesh P, Maisara S R S, Moniruzzaman M, Cecilia W, Sourav M, Kyaw T and Bidyut B S 2017 Ionic liquid as a new binder for activated carbon based consolidated composite adsorbents *Chem. Eng. J.* **326** 980-986

[7]   Cheng H, Ping W, Luo J, Jan F, Dirk E D V and Luo Z H 2015 Poly (ionic liquid)-based nanocomposites and their performance in CO_2 capture *Ind. Eng. Chem. Res.* **54** 3107-3115

[8]   Jianbin T, Huadong T, Weilin S, Henry P, Maciej R and Shen Y 2005 Poly(ionic liquid)s: A new material with enhanced and fast CO_2 absorption *Chem. Commun.* **0** 3325-3327

[9]   Hamayoun M, Hafiz M A S, Moniruzzaman M and Suzana Y 2016 Synthesis of ionic liquid polymer incorporating activated carbon for carbon dioxide capture and separation *Adv. Mater. Res.* **1133** 566-570

[10] Siriwardane R V, Shen M S and Edward P F 2005 Adsorption of CO_2 on zeolites at moderate temperatures *Energ. Fuel.* **19** 1153-1159

[11] Petrov I and Michalev T 2012 Synthesis of zeolite A: A review. Zlatarov University 1-5

[12] Yang H., Xu Z, Fan M, Gupta R, Slimane R B, Alan B E and Wright I 2008 Progress in carbon dioxide separation and capture: A review *J. Environ. Sci.* **20** 14-27

[13] Jadhav P, Chatti R V, Biniwale R B, Labhsetwar N K, Devotta S and Rayalu S S 2007 Monoethanol amine modified zeolite 13X for CO_2 adsorption at different temperatures *Energ. Fuel.* **21** 3555-3559

[14] Ojumu T V, Du Plessis P W and Petrik L F 2016 Synthesis of zeolite A from coal fly ash using ultrasonic treatment-A replacement for fusion step *Ultrason. Sonochem.* **31** 342-349

[15] Mojtaba M, Babak M, Alireza B and Ali S 2018 Solubility of carbon dioxide and methane in 1-hexyl-3-methylimidazolium nitrate ionic liquid, experimental and thermodynamic modeling *The J. Chem. Thermodyn.* **122** 31-37

[16] Franciele L B, Rafael B D, Marisol F R, Maria C C F, Luz A C, Vitaly V C, Felipe D V and Sandra E 2018 Cellulose based poly(ionic liquids): Tuning cation-anion interaction to improve carbon dioxide sorption *Fuel* **211** 76-86

[17] Andre B, Jianbin T, Hu X, Sugata P T, Youqing S and Maciej R 2007 Carbon dioxide solubility in polymerized ionic liquids containing ammonium and imidazolium cations from magnetic suspension balance: P[VBTMA][BF4] and P[VBMI][BF4] *Ind. Eng. Chem. Res.* **46** 5542-5547