



Carbon dioxide capture by ionic liquid in a membrane contactor

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ABSTRACT The emission of CO_2 due to burning of fossil fuel results in increasing the concentration of CO_2 in the atmosphere leading towards global warming. The ionic liquid was impregnated in the lords of membrane and contacted with flue gas containing CO_2 in counter flow at different temperature, flowrates and pressure. It has been predicted that by the end of 2030 the emission of CO_2 can reached up to 40.2 Gt. Membrane technology is an emerging technology used to capture CO_2 from flue gases. The current work is focused to analyze ionic liquid for capturing for post-combustion CO_2 through hydrophobic non-selective membrane in membrane contactor under low or atmospheric pressure. Slight pressure is applied only to maintain the interface stable between feed and ionic liquid phases. The ionic liquid was impregnated in the lords of membrane and contacted with flue gas containing CO_2 in counter flow at different temperature, flowrates and pressure. The feed gas in ratio of $\text{CO}_2:\text{N}_2$ was fed on one side of membrane while ionic liquid mixed with water in, was fed on the other side of the membrane. It has been observed that 1-butyl-3-methyl imidazolium *p*-toluenesulfonate ([Bsmim][TOS]) shows better selectivity. Moreover, as increase in flowrate and temperature showed the decrease in CO_2 capture efficiency.

Keywords: Membrane contactors, Ionic liquids, CO_2 capture, hydrophobic membrane.

1. INTRODUCTION

Carbon dioxide is consider of the main greenhouse gas which has ability to absorb and emit solar radiation coming directly from the sun^[1]. These radiations are responsible for increasing temperature of the earth surface^[2]. Greenhouse gases are also important for keep the planet temperature suitable for living^[3]. It has been estimated that without greenhouse gases the temperature of the earth would be -18 degree Celsius^[4].

With the growth of industrial revolution, fossil fuels based powered consumption rapid increase the emission of CO_2 ^[5]. This disordered the cycle of environment and increase the global temperature. This increase in the global temperature has termed as “global warming” and it have adverse effects on the globe in the shape of floods, heatwaves, and storms etc^[6]. In this regard the capturing of CO_2 before release to atmosphere is essential. There three modes of CO_2 capture i.e. *Pre-combustion, oxyfuel combustion capture and post-combustion capture*^[7].

Post-combustion technology is the mostly used technology as it can be retrofitted in existing plants and can be applied to both power plants and industrial sites. As the name suggest the CO_2 capture is performed after burning of fuels^[8]. This process is quite simple, firstly the fuel is injected in boiler where it burns with oxygen^[9]. The generated heat produce in boiler by burning can be used for various purposes such as industrial heating processes and electrical generation^[10]. This combustion also generate a flue gas mostly consist of water and carbon dioxide and nitrogen which ultimately flows into absorber tower from the bottom. As the gases rises up in the tower the liquid solvent is added from the top reacting with CO_2 contained in the flue gases. It creates a solvent- CO_2 solution which sinks into a column and leave absorber from the bottom while the rest of the flue gases leaves from the top^[8]. The solution of solvent- CO_2 is pumped into another column called stripper tower where solution is heated up to about 120°C causing the separation between the solvent and CO_2 ^[11]. The solvent is recollected at the bottom of the column to be reuse and CO_2 leaves from the top of the column and collected to be compressed. This technique captures about 90% of CO_2 produced and of all CCS (carbon captured and storage) technology this process achieved the highest degree of purity for carbon dioxide capture. In modern world of technology, this method is widely used as does not required fundamental changes to the plant processes. On the other hand, this is an energy intensive method which reduces the overall efficiency of the power plants by reducing the electricity output by more than 30%^[12].

Post-combustion technique has several subcategories such as absorption, adsorption, microbial (algal), membrane and cryogenics^[13]. As discuss above the process of absorption where amine/ammonia based solvents are used to capture CO_2 from the flue gases^[14]. In absorption process to capture CO_2 many solvents has been used. The attraction of CO_2 toward amines is greater^[15]. Moreover, the high thermal stability, and providing high space for CO_2 , amine hold strong position in absorption processes for CO_2 capture^[16]. Among all amine groups, monoethanolamine (MEA), tertiary amines such as methyl diethanolamine (MDEA), and sterically hindered amines such as 2-amino-2-methyl-1-propanol (AMP) are common absorbents for CO_2 capture system. However, the use of amines have several disadvantages i.e. higher regeneration energy requirements, corrosive in nature, high construction rate and degradability by SO_2 , NO_2 and O_2 in the flue gases^[17]. To overcome these issues several studies have been conducted. In the outcomes of recent researches proposed the ionic liquids to be the best replace of amines^[18]. The negligible vapor pressure, high thermal stability, high absorption capacity for CO_2 , non-

corrosive in nature and low regeneration cost have the properties of ionic liquids which makes it energetic alternative for CO₂ capture technologies^[19]. Few general properties of ionic liquids are listed in Table.1

Properties	General characteristics
A salt	Cation and anion quite large
Melting point	Below 100 °C
Boiling point	Greater than 200 °C
Thermal stability	Usually high
Viscosity	Less than 100 cP, workable
Dielectric constant	Less than 30
Polarity	Moderate
Specific conductivity	Less than 10 cS/cm 'Good'
Vapor pressure	Negligible
Solvency	Strong
Catalytic character	Best for several organic reactions.

Table.1 General characteristics of ILs^[20]

The strong intermolecular forces in ionic molecules make it strong enough that the vapor pressure is negligible at room temperature^[21]. Furthermore, the physiochemical properties of ILs can be tuned by adjusting cations and anions^[22]. As well as environmental concern, ILs are nonvolatile, non-flammable and recyclable which makes it environmental friendly as compared to amines^[23].

In the method of post-combustion, membrane technology has indulged which provides area for the ILs to improve the efficiency CCS technology^[24]. Membranes utilize differences in diffusivity, solubility, absorption abilities of different gases on different materials for separation. The performance of membrane depends upon several factors such as thickness of membrane, pore size, material of membrane and design of capture system^[25]. The operating cost of membrane is low. In addition, membrane can be utilized in both pre and post-combustion modes. Several other advantages of membranes are its low maintenance requirements, stability, light in weight and can be used vertically as well as horizontally^[26].

Many researchers including Park et al., Bernardo et al., Brunetti et al., Ebner and Ritter, Khilipour et al., Kotowicz et al., and Atsonions et al., emphasize on recent development of membrane technology for CO₂ capture. Kotowicz et al. used membrane in his several studies to its impact in CCS. Burdyny et al. used membrane in the study of availability of hybrid separation. Luis et al. classified membranes on the basis of their separation mechanism totally depend upon the performance of membrane as the function of material used.

Polymeric membranes are the membrane which have variety of commercial applications^[24]. The two types of polymeric membranes are fully dependent upon the glass temperature of the membrane. The examples of glassy polymers are polysulfones, polyimides, polyaramides and polycarbonates which are most common in their applications^[27]. The polymer, polyethylene oxide contains ether group which is polar in nature. This polarity makes it quadrupolar interaction for CO₂. Recent studies have shown that this polymer has higher affinity toward CO₂^[28].

Hollow fiber membrane is mostly used in membrane contactor as non-selective barrier between liquid-gas and gas-gas phases in cross flow as well as in parallel flow^[24]. Along with polyethylene oxide, polyvinylidene fluoride (PVDF) are the best candidate for the liquid-gas separation due to its high selectivity, permeability, and strong affinity toward CO₂^[29]. The unique properties of ILs with PVDF combine can enhance the selectivity of CO₂ from the flue gases. In the solubility of CO₂ in ILs, anion plays its primary role while cations played secondary role. Cadena et al. studied the molecular structure of ILs for the solubility of CO₂^[27]. The author conducted an experiment with imidazolium based cation. Two anions (BF₄ and BF₆) were linked with imidazolium separately. According to data the interaction between ILs is Lewis acid-base type in which anion behaves as Lewis base and CO₂ as Lewis acid. Furthermore, spectroscopic results suggested that the attraction of CO₂ for the BF₄ is greater than BF₆. This means that CO₂ molecules penetrate into the void spaces of ILs. CO₂ solubility highly depends upon the number of fluoro groups as the number of fluoro group increases the solubility of CO₂ increases in following order^[30]:

[BF₄] < [TFO] < [TFA] < [PF₆] < [Tf₂N] < [methide] < [C₇F₁₅CO₂] < [Etap] < [bFAP].

This research is based on experimentation work for the absorption of CO₂ with ionic liquids impregnated on PTFE facilitated in membrane contactor. The high binding capacity, high mechanical strength, and chemical resistance of the PTFE membrane makes it the best area provider for 1-butyl-3-

methyl imidazolium p-toluenesulfonate ([Bmim][TOS]) and N-butyl-4-

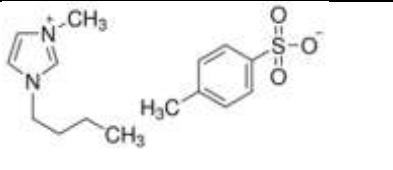
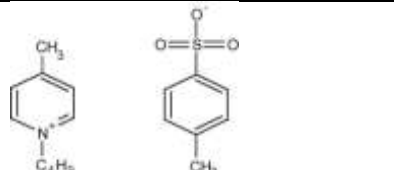
Ionic Liquids	1-butyl-3-methyl imidazolium ρ -toluenesulfonate	<i>N</i> -butyl-4-methylpyridinium tosylate
Abbreviation	[Bmim][TOS]	[BMPY][TOS]
Structure		
Melting point	67 °C	51.7 °C
CAS number	410522-18-8	880143-38-4
Molecular formula	C ₁₅ H ₂₂ N ₂ O ₃ S	C ₁₇ H ₂₃ NO ₃ S
Molecular weight	310.41	321.43400

Table 2.1: Chemical structure, abbreviation and name of ionic liquids^[31]

methylpyridinium tosylate ([BMPY][TOS]). A 2D model was developed to study the separation of CO₂ from flue gases at different flow rates, pressures and temperatures.

2. EXPERIMENTATION

2.1. Material

Ionic liquids 1-butyl-3-methyl imidazolium ρ -toluenesulfonate ([Bmim][TOS]) and *N*-butyl-4-methylpyridiniumtosylate ([BMPY][TOS]) were purchased from Guangzhou Green Trading company limited, China. Cylinders of Carbon dioxide (98%) and Nitrogen (99%) were also purchased from Sales Instock Pakistan. Ionic liquids with their chemical structure, name, abbreviation and some other important properties are given in table 2.1. Both of these ionic liquids are selected for the CO₂ capturing due to their high stability to temperature. The anions of these ionic liquids are same i.e. [TOS] and cations are imidazolium and pyridinium based. Moreover, the non-volatility of these ionic liquids make them best solvents for CO₂ in hollow fiber membranes. The melting point of [Bmim][TOS] is 67 °C and [BMPy][TOS] is 57.1 °C which further make them best absorbents for CO₂.

Polytetrafluoroethylene (PTFE) was purchased from Hannah Han Jiangsu Benenv Environmental Technologies Co., Ltd, China.

2.2. Method

Under various condition the absorption capacity of PTFE impregnated with ionic liquid in membrane contactor for CO₂ is studied.

First; Nitrogen and carbon dioxide is mixed to prepare a sample of flue gas. The composition of prepared flue gas was according to the pressure of nitrogen and carbon dioxide. The composition of prepared flue gas was made nitrogen 70% and carbon dioxide 30% according to the composition of flue gas.

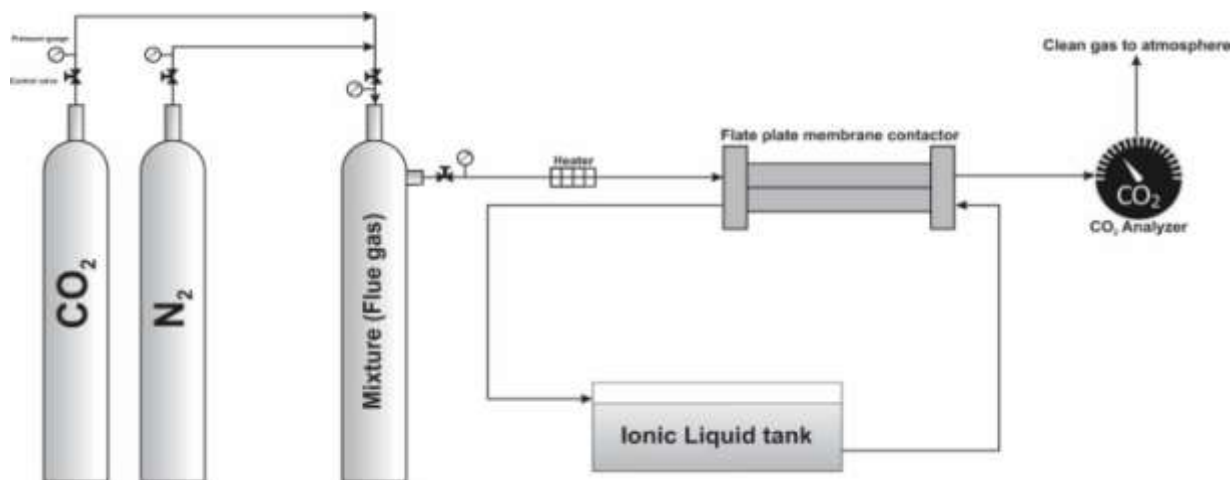


Figure 2.1: Experimentation setup of flatplate membrane contactor for CO₂ capture

Second; a stream of prepared flue gas is connected membrane contactor by passing a heat exchanger to increase the temperature of flue gas up to 50–55 °C. Membrane contactor is facilitated with PTFE membranes separately for separate experiments to study its effect in capturing carbon dioxide by flowing ionic liquids solution in a cross flow to flue gas. Hence three important agents are utilizing to capture carbon dioxide i.e. membranes, ionic liquids and membrane contactor.

Thirdly; two different Ionic liquids solution were prepared of two ionic liquids i.e. 1-butyl-3-methyl imidazolium *p*-toluenesulfonate ([Bmim][TOS]) and N-butyl-4-methylpyridinium tosylate ([BMPY][TOS]) separately for testing of separation of CO₂. The ionic liquids are the molten salts and its melting point is low due to which it exists in molten form even at room temperature. The viscosity of ionic liquid is low but to make it able to flow freely through flat plate membrane contactor it must be mixed with water. 50 grams of ionic liquids mixed with half liter of water. These all three important arrangements are linked with each other. The experimentation setup is given in figure 4.5.

Initially the flue gases with nitrogen (85%) and carbon dioxide (15%) was passed with the flow rate of 50 ml min⁻¹ and flow rate of ionic liquid was adjust at 50 ml min⁻¹. The flow rate of ionic liquids was kept constant over entire experimentation and the flow rates of flue gases was changing from 50 to 100 ml min⁻¹. Each flow rate was studied for 10 minutes and at the end of 10 mints the flue gas was studied with the help of gas analyzers. More over the flue gases at 50 ml min⁻¹ was also studied at different temperatures.

The flux of CO₂ absorption and for experimental overall mass transfer coefficient is calculated by the equation:

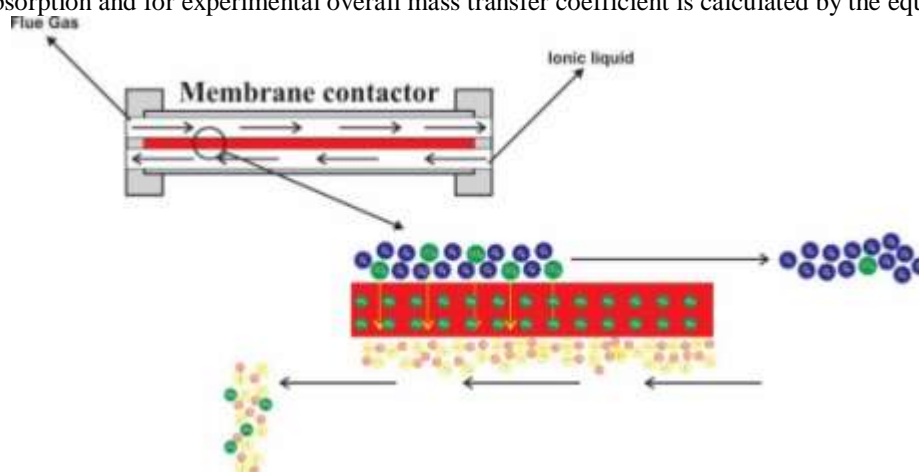


Figure 2.2: Schematic diagram of flat plate membrane contactor

$$j_{CO_2} = \frac{(Q_{g-in})(C_{g-in}) - (Q_{g-out})(C_{g-out})}{A} = K_{exp} \Delta C_g \quad (1)$$

$$\Delta C_g = \frac{C_{g-in} - C_{g-out}}{\ln\left(\frac{C_{g-in}}{C_{g-out}}\right)} \quad (2)$$

Q_{g-in} and Q_{g-out} is the flow rate of gas inlet to membrane contactor and gase outlet from membrane contactor, C_{g-in} and C_{g-out} is the concentration of gases at inlet of membrane contactor and outlet of membrane contactor respectively. Whereas, the mean of driving force is represented by equation 2.

Permeance is the property of a membrane to allows materials to pass through it. The membrane permeance is given by equation 4.2.

$$j(\text{permeance}) = \frac{DS}{l} \quad (3)$$

D represent diffusivity coefficient, S is solubility coefficient and l represents membrane thickness.

Permeability of PTFE was found by passing pure flue gas over it in membrane contactor with the counter flow of ionic liquids. Table 2.3 have the collected data of pure flue gas permeability and selectivity.

Ionic Liquids	Permeability of CO ₂	Permeability of N ₂
[BMPY][TOS]	27.74	0.35
[Bmim][TOS]	28.94	0.33

Table 5.1: Permeability of CO₂ and N₂ and selectivity of PTFE

3. Results and Discussions

Two ionic liquids 1-butyl-3-methyl imidazolium ρ -toluenesulfonate ([Bmim][TOS]) and N-butyl-4-methylpyridinium tosylate ([BMPY][TOS]) have been studied for the separation of carbon dioxide at PTFE membrane. The aim of this experimentation is to study the solubility of CO₂ in ionic liquids through a barrier of PTFE membrane. Moreover, this experimentation also give the selectivity of CO₂ in ionic liquids at different flow rates of flue gas and variable temperature.

3.1. Permeability vs Flow rate

Figure 3.1 shows the comparison of permeability of a set of PTFE membrane impregnated with two different ionic liquids. The experiment is conducted with a variable flow rate from 50 to 100 ml min⁻¹. The permeability trend for both ionic liquids impregnated on the PTFE membrane goes on decreasing at the given range of the flow rate. Initially, the permeability of [Bmim][TOS] was recorded 87.69 and permeability of [BMPY][TOS] was recorded 79.25 respectively. At maximum flow rate the flow rate of [Bmim][TOS] and [BMPY][TOS] was 45.91 and 9.77 respectively. The decline in the value of permeability of [Bmim][TOS] is higher than [Bmim][TOS]. As we increase the flow rate the membrane became wet and the pores of the membrane is filled with the traces of the CO₂ and N₂. This results in the decrease of the permeability.

3.2. Efficiency vs Flow rate

Efficiency is depend upon the permeability of the membrane^[32]. We already discussed that with increase flow rate the permeability of the membrane decreasing due to membrane wetting and pores of the membrane filled with the traces of the CO₂ and N₂. This directly effect the efficiency of the process of CO₂ separation from the flue gas. Figure 3.2 shows the trend of the efficiency of the two PTFE membrane impregnated with two ionic liquids.

3.3. Flux vs Flowrate

Flux of flue gases also decreased with increasing flow rate. This is because of the reasons due to blockage of pores. Figure

3.3 shows the trend of the flux vs flowrate.

3.4. Permeability vs Temperature

Generally, the solubility of gases decreases with the increase of temperature^[33]. Similar case with the flue gases. The conducted experimentation for the captured of carbon dioxide from the flue gases was initially pass through the membrane conductor at 60 °C. The flow rate was kept constant at 50 ml min⁻¹ at both ends of membrane contactor. The observed data in table 5.4 collected after every 10 degree Celsius temperature interval after 10 minutes. Figure 3.4 shows the trend of permeability with variable temperature.

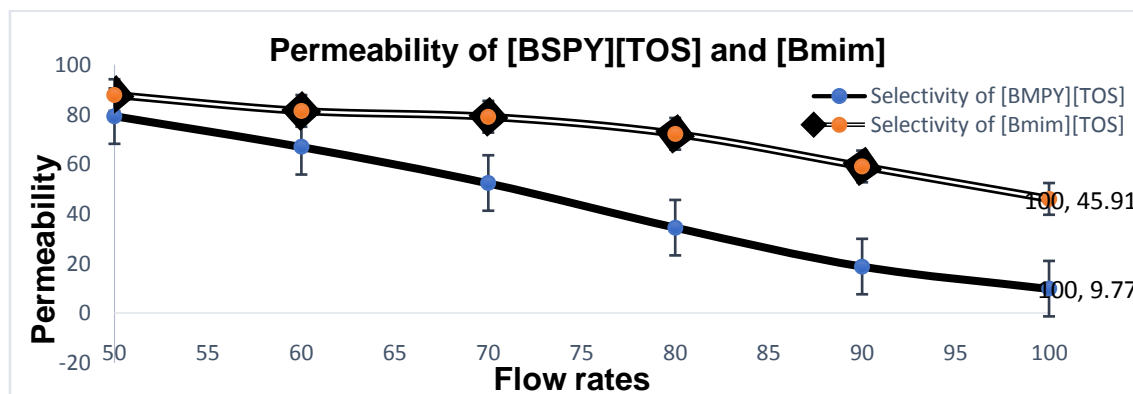


Figure 3.1: Permeability of ionic liquids for variable flow rate of flue gas

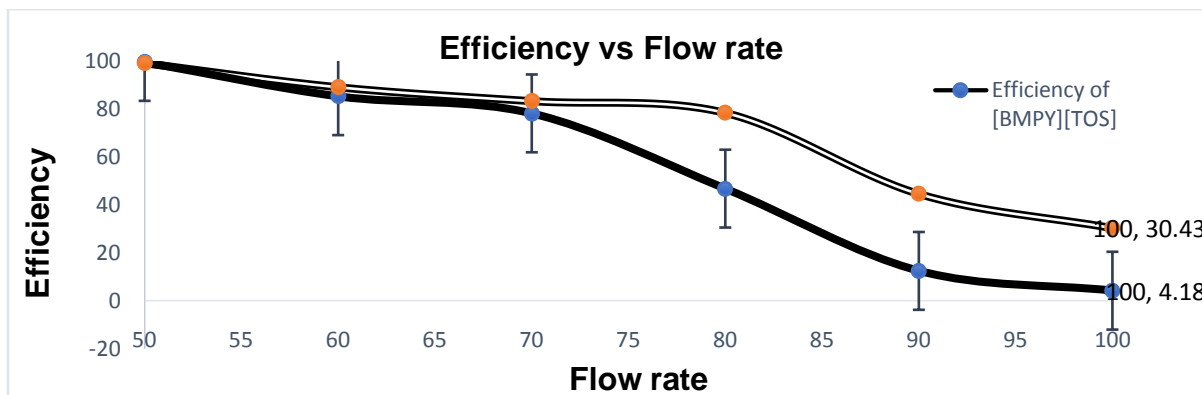


Figure 3.2: Efficiency of ionic liquids for variable flow rate of flue gas

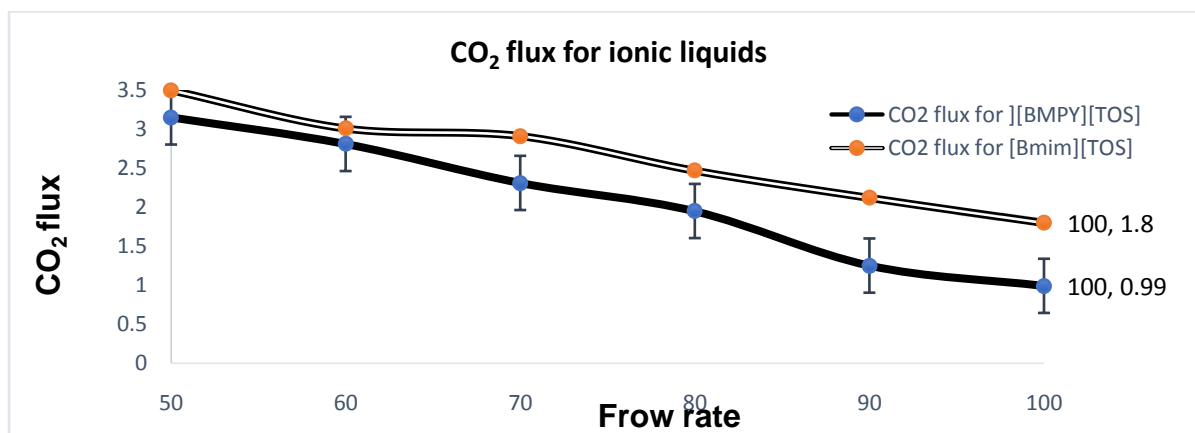


Figure 3.3: CO₂ flux for ionic liquids for variable flow rate of flue gas.

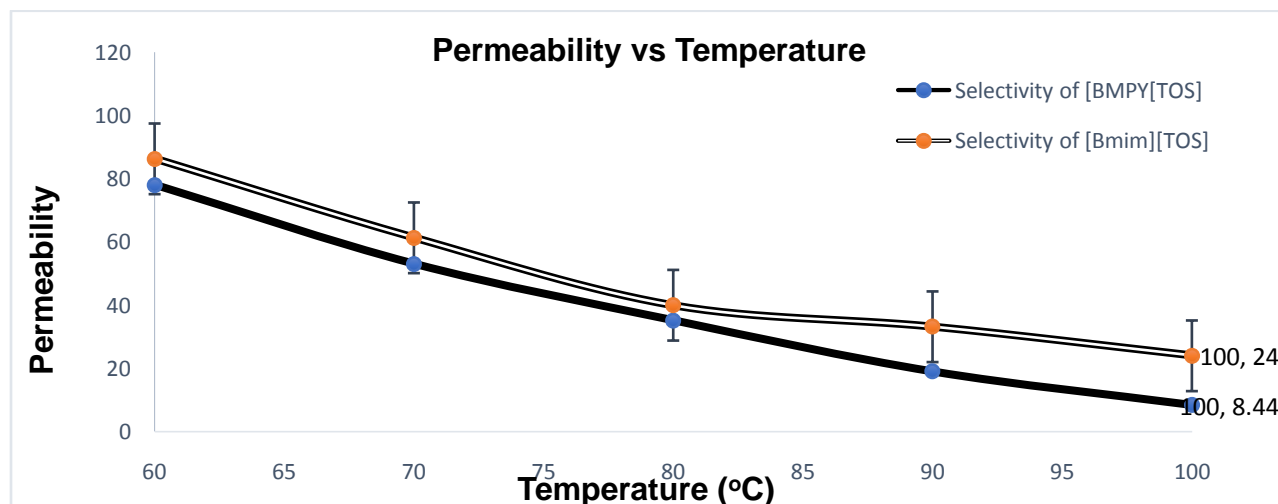


Figure 3.4: Permeability of ionic liquids at different temperature

4. CONCLUSION

Absorption of ionic liquids are depend upon cations and ions. The Ion plays primary role, in the selected ionic liquids i.e. [BMPY][TOS] and [Bmim][TOS] have the same anion and different cations. The cation [Bmim] shows greater attraction toward CO₂ than [BMPY] because [Bmim][TOS] contain imidazolium based cation. Overall absorption through PTFE membrane was greater than that of previous performed experiments without ionic liquids.

The efficiency of CO₂ captured was not remained same and was reducing with time. The reduction in efficiency was due to several factors. First, the membrane wetting caused the reduction in efficiency. Second, the available ionic liquids get

concentrated as it circulated through membrane contactor. Third, as the temperature increases the the glass temperature of membrane approaching and it effect the working capability of membrane.

The flux also reduced during experimentation using both the ionic liquids. The reason for the reduction of flux was due to the pores get stacked with particles of CO₂ and N₂. It cause decreasing in the permeability of membrane. Hence the flux reduces. Overall, ionic liquids has shown greater attraction in capturing CO₂ from flue gases. The conventional methods for CO₂ capturing are not only expensive but corrosive in nature too. Thus Ionic liquids provide a space for high efficiency of CO₂ capture with least regeneration energy cost and can be used again and again

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