Ionic Liquid Solvents as Advanced Treatment Method for CO$_2$ Control: A Review Research

Shumous S. Sayar$^1$, Thamer J. Mohammed$^1$ and Abdul Mun'em Abbas Karim$^2$

$^1$Chemical Engineering Department, University of Technology, Baghdad, Iraq.
$^2$Chemical Engineering Department, College of Engineering, University of Diyala, Diyala, Iraq.
E-mail: che.19.12@grad.uotechnology.edu.iq

Abstract. Climate change issues have risen in recent years due to human activities produce carbon dioxide (CO$_2$) emissions. By 2021, the Intergovernmental Panel on Climate Change predicts a temperature increase of 1.9°C. CO$_2$ reduction is crucial for humans and all other forms of life on Earth. To mitigate this potential issue, immediate improvements in CO$_2$ separation processes are needed. One of the most efficient methods in separating it is to use water amine chemical absorption as an ionic liquid solvent. Therefore, this paper addresses common solvents used in this respect, such as alkanolamine, ionic liquid and their mixed aqueous solutions in the absorption process. The success factors in the mass are the transfer phenomenon between CO$_2$ and solvent. The physical factors were examined, and the chemical properties of liquid ionic solvents were examined.

Keywords: hydrodynamics; mass transfer; carbon dioxide absorption; ionic liquids; flue gas

1. Introduction

Over the last century, industrialization and population growth have resulted in more pollution. Air pollution is the most pressing problem in the environmental debate, apart from contamination of water and soil, which has a detrimental effect on the ecosystem. One of the most common waste gases released by factories, industrial plants, and vehicles is carbon dioxide (CO$_2$). The greenhouse effect, which triggers rising temperatures, is the most important problem with carbon dioxide. Carbon dioxide is to blame for more than 60% of global warming. According to scientific estimates, CO$_2$ concentrations are now around 400 ppm, a substantial rise from their pre-industrial levels of less than 300 ppm. By 2100, the Intergovernmental Panel on Climate Change (IPCC) predicts a 1.9°C rise in global temperature, meaning that reducing CO$_2$ levels is important for humans and all other life on the planet; health problems, urban smog, and acid rain are only a few of the major implications of CO$_2$ pollution. Several options are proposed for reducing total CO$_2$ in the atmosphere. The first is to substitute fossil fuels with non-carbon energy resources such as wind and solar energy and biomass, which necessitates switching to non-fossil fuels (e.g. renewable energy and hydrogen). The second solution is to improve energy efficiency to reduce greenhouse gas emissions per unit energy consumption, which requires efficient energy use. The third is carbon capture and storage (CCS).

Advanced solvents, such as ionic liquids (ILs), have been touted as potential CO$_2$ capture candidates. Paul Walden discovered the first IL (ethyl ammonium nitrate) in 1914, but he had no idea that ILs would become a major scientific field almost a century later. In reality, ILs have only recently gotten a lot of attention as creative fluids. The number of SCI papers published on ILs has risen exponentially, from a few in 1996 to >5000 in 2016, far outpacing other prominent science fields' annual growth rates. This fact indicates that an increasing number of researchers are working on this fascinating subject, with a plethora of results. ILs are the subject of a multidisciplinary study involving chemistry, materials science, chemical engineering, and environmental science. As more information about the essence of ILs becomes accessible, some key fundamental views have begun to diverge from the original principles.[1][2]
2. CO₂ capture technologies
Different technologies have been used to extract CO₂ from flue gas in industries such as petroleum, chemical, and traditional fossil fuel-fired technology. These technologies include chemical absorption, physical adsorption, cryogenic processes, membrane isolation, and biological fixation. The various technological options for CO₂ capture from flue gas are depicted in Figure 1. These options can be found under the headings of absorption, adsorption, membranes, cryogenic, and microalgal.[3]

Figure 1: CO₂ capture technologies [4]

3. Conventional ionic liquids for separating CO₂
Research has relied on measuring the impact of variables such as pressure, temperature, and selection of anions/cations over the last decade and until now. The results indicated that the solubility of carbon dioxide was high in so-called conventional ionic liquids. They are defined as ILs that do not have a functional group associated with them, and many report that they reflect the typical physical solvent behaviour [5,6]. This behaviour is evidenced by low-pressure carbon dioxide (1-2 bar) contact with IL, which leads to a decrease in the concentration of liquid phase carbon dioxide. As the pressure rises, the concentration of absorbed carbon dioxide rises, generally up to 100 bars. Hence, the general characteristics of physical absorption are manifested. As a general rule, the solubility of carbon dioxide in IL increases with increasing pressure and decreases with increasing temperature. The physical absorption process is the product of the exchange of carbon dioxide occupying "free space" in the IL structure through large molecules and IL. The carbon dioxide momentum is quadrupole and van der Waals forces.

3.1. Effect of cations on the CO₂ absorption
Among the many potential interest properties [7][8], ionic liquids (IL) exhibit unique carbon dioxide absorption properties. [9] Although they dissolve carbon dioxide much better than other gases, Brennick and colleagues explained, [10] they are virtually insoluble in supercritical carbon dioxide, making them ideal candidates for more than just capturing carbon dioxide from gases. Industrial waste, [11][12], Extraction processes[8] and two-phase or multi-phase catalysis with the presence of
carbon dioxide and gas separation. [9] The solubility of carbon dioxide needs to be understood by defining the sites of reaction between CO\textsubscript{2} and IL in order to enhance these applications. [12] Several experimental studies have therefore been carried out to compare the constants of Henry's law for different ILs [8][10][13][14][15], and an image of the CO\textsubscript{2} solution in IL has been generated based on the observed patterns, which can be verified by the corresponding theory [8][13]-[16]. These studies' general knowledge is that the interaction between the cation and carbon dioxide is somewhat constrained by the side chain's small contribution [14]. However, the anion plays a critical role in the solution-solvent interaction, and this has still not been stated any big direct influence of a supportive group of heads. The formation of an imidazolium-based hydrogen bond [17]-[19] in an IL between the oxygen atoms of CO\textsubscript{2} and the hydrogen atoms of the cationic ring was therefore excluded since the constants of Henry's law did not change in the experiments and none of them altered the discrepancy in the solvent's microscopic composition. It is inferred that the cation is negligible in the classical modelling of molecular dynamics (MD) by swapping the most acidic (and thus the most reactive) H atoms for the methyl group [13].

3.2. Effect of Anions on the absorption of CO\textsubscript{2}

The carbon dioxide anion reaction can be described as a Lewis acid-base reaction, so this reaction becomes stronger as the anion increases. Interestingly, the formation of carbohydrates can also occur in the presence of basic anions due to the proton's transfer from the cation to the anion[20]-[23]. And since it is established that carbohydrates interact with the carbon dioxide formed by imidazolium carbonate[24], the basic anions are assumed to be sufficient to shape such structures. The chemical absorption of carbon dioxide in 1,3-dialkyl imidazolium acetate was suggested by agreement based on a substantial increase in the solubility of carbon dioxide in these ILs[25] and Rogers et al.[26] (and subsequently several other groups)[27,30] In the same method, 1,3-imidazolium carboxylate was recently developed. In these ILs, carbon dioxide's physical absorption into 1,3-dialkyl imidazolium acetate followed by a carbine solution reaction may be available. However, a more thorough understanding of each phase of the process's dynamics is needed to refine and use this interaction more efficiently. The physical absorption of carbon dioxide into 1-ethyl-3-methylimidazolium acetate ([C\textsubscript{2}N\textsubscript{2}Et][OAc]) is preliminarily investigated in this theoretical research as the first set of studies of this apparently fascinating yet very complex method. Also, an improved interaction of the anion with carbon dioxide can be predicted due to the acetate anion's greater basicity. Consequently, the role of cation in the dissolution of carbon dioxide in this system should be lower, allowing an accurate understanding of the nature of interactions in IL between cation and carbon dioxide-based on imidazolium as a whole to be obtained.

3.3. Effect of Temperature on the absorption of CO\textsubscript{2}

In general, temperature has a significant impact on reaction kinetics and, as a result, mass transfer. As for the kinetics of carbon dioxide absorption, The constant reaction rate is generally associated with the Arrhenius expression [5]:

\[ k = Ae^{−E_a/RT} \]  \hspace{1cm} (1)

Where:-
- \( k \) = rate constant
- \( A \) = pre-exponential factor (in joule/mole)
- \( E_a \) = activation energy (in kJ/mole)
- \( R \) = universal gas constant (in J/mol.k)
- \( T \) = absolute temperature (in kelvins)

In the following statement, the normal log of the equation ends:

\[ \ln(k) = \ln(A) - \frac{E_a}{R} \frac{1}{T} \]  \hspace{1cm} (2)
This equation shows that a higher temperature results in a constant higher rate and a higher transfer rate. In the meantime, some researchers have shown that very high temperatures reduce efficiency, and they show that absorption efficiency decreases as the temperature increases from 36 °C to 45 °C. This reduction was due to the exothermic CO₂ absorption thermodynamic mechanism, which could lead to undesirable reactions at too high a temperature. An increase in temperature will lead to a decrease in physical solubility. As the temperature changes, there must be a balance between kinetic melting of the reaction and physical melting. As the temperature rises, kLa increases dramatically from 293 to 336 K. Temperature increases decrease viscosity, thus increasing the flow and mixing of gas and liquid; thus, kLa increases sharply; on the other hand, the diffusion coefficient is temperature-proportional and viscosity-inversely proportional. The higher temperature facilitated the diffusion of carbon dioxide into the ionic liquid, increasing kLa.[5]

4. Task-Specific Ionic Liquids for CO₂separation

Bates et al. [31][32] first proposed the notion of a special ionic liquid or ionic liquid feature (TSIL). The authors functionalized the imidazolium cation with the primary amine gap in this research. As shown in Figure 1, this new TSIL has been shown to react with carbon dioxide at a stoichiometric ratio of 2:1. It should be noted that this stoichiometry is close in the carbamate formation scheme to the theoretical maximum molar absorption of carbon dioxide by common amines. Evidence is presented in Fig.2 for carbamate formation. FT-IR and NMR tests of ionic fluids treated with CO₂ and untreated CO₂ were presented. In addition, the authors report that the reaction was reversible and when heated (80-100 °C) in a vacuum for several hours, carbon dioxide could be released. While the authors noticed that the composite ionic liquid had a relatively high viscosity, they did not observe a sharp increase in viscosity following carbon dioxide's reaction to TSIL.

![Figure 2: Reaction between the functionalized ionic liquid from the cation and CO₂. In a 2:1 stoichiometry, the IL interacts with CO₂ forming a carbamate salt.][31]

5. Conclusion

From an economic and environmental point of view, one of the most promising CO₂ innovations has been proposed because of IL’s unique characteristics. Many advantages exist for common solvents, including high reactivity, high absorption rates, low reaction temperatures, low corrosion, and suitability for modern technology. However, it was also stressed that these solvents have several drawbacks, including solvent degradation, erosion, high level of energy, high volatility and limited use, as well as slow reaction, so that ionic liquids, their wide range of liquids, their thermal stability, were referred to as new alternative solvents. Low heat strength, low vapour pressure, controlled physicochemical characteristics and high solubility of carbon dioxide, imidazolium-based ionic liquids (such as [bmim] [BF4], [bmim] [PF6] and emim] [Tf2N]) have been described in this report. A typical
ionic liquid structure has been described and proposed as an effective blend with another common solvent. Furthermore, TSILs such as [Am-Im][BF4] and [Am-Im][DCA] were also created to show the solvents’ considerable potential. The coefficient of mass transfer can also be affected by viscosity and other physical properties. However, The relationship between the physicochemical properties of ionic liquids and their mixtures and mass transfer coefficients is still poorly understood. However, more knowledge is needed on the relationship between mass transfer and the physicochemical properties of ionic liquids, TSILs, or their mixtures. It should, therefore, be investigated in the near future.

References
[1] Haines A, Kovats R, Campbell-Lendrum D and Corvalan C. 2006 Climate change and human health: impacts, vulnerability and public health. Public Health; 120: 585–96.
[2] Grimston MC, Karakoussis V, Fouquet R, van der Vorst R, Pearson P and Leach M 2001 The European and global potential of carbon dioxide sequestration in tackling climate change. Clim Policy; 1: 155–171.
[3] Choi WJ, Seo JB, Jang SY, Jung JH and Oh KJ 2009R emoval characteristics of CO2 using aqueous MEA/AMP solutions in the absorption and regeneration process. J Environ Sci; 21: 907–913.
[4] Rao AB and Rubin ES 2002 A technical, economic, and environmental assessment of amine-based CO2 capture technology for power plant greenhouse gas control. Environ Sci Technol 36: 4467–75.
[5] Kenarsari SD, Yang D, Jiang G, Zhang S, Wang J, Russell AG, Wei Q and Fan M 2013 Review recent advances in carbon dioxide separation and capture. Rsc Adv 3(45):22739–73
[6] Baltus RE, Culbertson BH, Dai S, Luo H and DePaoli DW 2004 Low-pressure solubility of carbon dioxide in room-temperature ionic liquids measured with a quartz crystal microbalance, TheJournalofPhysicalChemistryB,108(2), pp. 721–7.
[7] Lee BC and Outcalt SL 2006. Solubilities of gases in the ionic liquid 1-n-butyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide. Journal of Chemical & Engineering Data, 51(3), pp.892–7.
[8] Hallett JP and Welton T 2011 Chem. Rev.;111:3508–3576. [PubMed] [Google Scholar]
[9] Hunt PA and Kirchner B, Welton T. 2006 Chem. Eur. J.;12:6762–6775. [PubMed] [Google Scholar]
[10] Jutz F, Andanson J-M and Baiker A. 2011 Chem. Rev.;111:322–353. [PubMed] [Google Scholar]
[11] Blanchard LA and Hancu D 1999 Beckman EJ, Brennecke JF. N.;399:28–29. [Google Scholar]
[12] Anderson JL, Dixon JK, Brennecke JF. Acc. Chem. Res. 2007;40:1208–1216. [PubMed] [Google Scholar]
[13] Brennecke JF, Gurkan BE. J. Phys. Chem. Lett. 2010;1:3459–3464. [Google Scholar]
[14] Bhargava BL, Balasubramanian S. Chem. Phys. Lett. 2007;444:242–246. [Google Scholar]
[15] Cadena C, Anthony JL, Shah JK, Morrow TJ, Brennecke JF, Maginn EJ. J. Am. Chem. Soc. 2004;126:5300–5308. [PubMed] [Google Scholar]
[16] Almantariotis D, Stevanovic S, Fandino O, Pensado AS, Padua AAH, Coxam J-Y, Costa Gomes MF. J. Phys. Chem. B., 2012;116:7728–7738. [PubMed] [Google Scholar]
[17] Anthony JL, Anderson JL, Maginn EJ, Brennecke JF. J. Phys. Chem. B., 2005;109:6366–6374. [PubMed] [Google Scholar]
[18] Deschamps J, Costa Gomes MF, Padua AAH. ChemPhysChem. 2004;5:1049–1052. [PubMed] [Google Scholar]
[19] Skarmoutsos I, Dellis D, Matthews RP, Welton T and Hunt PA; 2012 J. Phys. Chem. B.;116:4921–33. [PubMed] [Google Scholar]
[20] Lehmann SBC, Roatsch M, Schöppke M and Kirchner B. Phys. 2010 Chem. Chem. Phys.;12:7473–86. [PubMed] [Google Scholar]
[21] Kempter V, Kirchner B J 2010 Mol. Struct.; 972:22–34. [Google Scholar]
[22] Hollóczki O, Gerhard D, Massone K, Szarvas L, Németh B, Veszprémi T, Nyulászi L. 2010 New J. Chem.;34:3004–9. [Google Scholar]
[23] Rodríguez H, Gurau G, Holbrey JD and Rogers RD 2011 Chem. Commun.;47:3222–4. [PubMed] [Google Scholar]
[24] Kelemen Z, Hollóczki O, Nagy J, Nyulászi L 2011 Org. Biomol. Chem.;9:5362–4. [PubMed] [Google Scholar]
[25] Hollóczki O and Nyulázi K 2012 Top. Curr. Chem. DOI: 10.1007/128_2012_416. [PubMed] [Google Scholar]

[26] Kuhn N, Steinmann M, Weyers G, Henkel G Z and Naturforsch B 1999 54:434–40. [Google Scholar]

[27] Shiflett MB and Yokozeki A J 2009 Chem. Eng. Data.; 54:108–14. [Google Scholar]

[28] Gurau G, Rodríguez H, Kelley SP, Janiczek P, Kalb RS, Rogers RD. Angew. Chem. 2011; 123:12230–2. [PubMed] [Google Scholar] Angew. Chem. Int. Ed 50:12024–6. [PubMed] [Google Scholar]

[29] Cabaço MI, Besnard M, Danten Y, Coutinho JAP 2012 J. Phys. Chem. A. 116:605–1620. [PubMed] [Google Scholar]

[30] Besnard M, Cabaco MI, Chávez FV, Pinaud N, Sebastiao PJ, Coutinho JAP, Mascetti J and Danten Y J 2012 Phys. Chem. A.;116:4890–4901. [PubMed] [Google Scholar]

[31] Besnard M, Cabaco MI, Chávez FV, Pinaud N, Sebastiao PJ, Coutinho JAP and Danten Y 2012 Chem. Commun.;48:1245–1247. [PubMed] [Google Scholar]

[32] Shiflett MB, Elliott BA, Lustig SR, Sabesan S, Kelkar MS and Yokozeki A. 2012 ChemPhysChem.;13:1806–1817. [PubMed] [Google Scholar]