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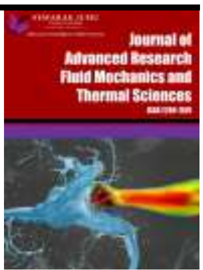

Green and Biodegradable ChAAILs for Enhanced CO_2 Capture: Insights from Water Content, Density, and Viscosity Analysis

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ABSTRACT

A major problem with the prevalent use of alkanolamines in conventional carbon capture technology is their inherent disadvantages, such as the demanding regeneration process, which involves high energy consumption, as well as the formation of toxic byproducts during degradation, which have triggered extensive research into alternative methods. An important area of research has focused on the development of green solvents as viable and sustainable replacements for traditional alkanolamine-based approaches. In this work, two cholinium amino acid-based ionic liquids (ChAAIL) were synthesized via the acid-base neutralization method. ChAAIL moieties were characterized using ATR - FTIR spectroscopy techniques. The high-water content of all ChAAIL ionic liquids confirmed the synergistic hygroscopic effect arising from both cholinium cations and amino acid anions. Thermophysical analysis data consisting of density and viscosity provide a better understanding of the correlation between the above properties and the molecular structure of ChAAIL. A thorough understanding of these novel ionic liquids is crucial for developing a greener and more effective green solvent for carbon capture and mitigation technology.

1. Introduction

Combating climate change and its associated impacts is one of the crucial goals among the 17 Sustainable Development Goals (SDGs) to be achieved by 2030. This global challenge is primarily caused by anthropogenic carbon dioxide emissions resulting from the burning of fossil fuels in various industrial sectors, which have a profound impact on our planet's delicate climate. Dependence on fossil fuels as a primary energy source remains a significant factor contributing to rising CO_2 concentrations in the atmosphere. In 2019, global CO_2 concentration reached alarming levels,

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reaching 409.18 0.1 ppm [1]. The relentless increase in anthropogenic CO_2 emissions, combined with the release of other greenhouse gases, has led to a worrying rise in global temperatures. As the World Meteorological Organization (WMO) [2] confirmed in its January 2021 press release, the global average temperature in 2020 exceeded pre-industrial levels by a remarkable 1.2°C.

Although conventional carbon capture and sequestration technology, which relies primarily on chemical absorption using alkanolamines, is mature, it is fraught with inherent problems. Alkanolamines exhibit low biodegradability and high ecotoxicity and corrosive properties that pose a significant threat to the environment and may cause irreversible damage [3]. The confluence of several factors, including the significant amount of alkanolamine required, the significant capital investment, the significant energy costs associated with solvent regeneration, and the environmental risks posed by commonly used alkanolamines make the overall chemical absorption CO_2 capture process unsustainable and environmentally burdensome [4-9].

Ionic liquids (ILs) are a family of molten salts that have melting temperatures below 100 °C and are made up of organic cations and organic/inorganic anions [10]. These substances offer unique physicochemical characteristics, such as low vapor pressure, low flammability, and outstanding thermal stability, that have attracted a lot of attention from the scientific community as green solvents [10-12]. Unfortunately, despite the ‘green solvent’ status, not all ionic liquids can be regarded as biodegradable. Numerous ionic liquids made from imidazolium and pyridinium do not adhere to the requirements for biodegradability, according to Hou *et al.,* [13] and Petkovic *et al.,* [14]. Ionic liquids (ILs) based on cholinium cation have attracted a lot of attention from scientists as prospective substitutes for traditional ILs because of their greater biodegradability and affordable production [13,15,16]. The main characteristic of cholinium cations is their proven low toxicity. They are identified by a quaternary ammonium structure with an attached hydroxyl group on the alkyl side. This property makes cholinium-based ILs an attractive choice for accelerating the development of ecological and biodegradable green solvents.

Amino acids are essential building blocks for protein inside of humans and animals. As bio – renewable material, anion that stemmed from amino acid groups would complement the cations selected in this study to improve the biodegradability aspect of the ionic liquid as well as facilitate the absorption of CO_2. Unlike conventional ionic liquid made of perfluorinated anions that capture CO_2 through physical absorption, the presence of amine group enabled the absorption of CO_2 through weak chemisorption interaction [17-19]. In this work, two different ChAAIL, namely cholinium L – alaninate ([Chl][Ala]) and cholinium L – serinate ([Chl][Seri]) were synthesized via acid – base neutralization method. The moieties of the ionic liquids were confirmed by using attenuated total reflectance Fourier – Transform infrared (ATR - FTIR) spectroscopy. The water content for all ChAAIL were analysed by Karl Fischer titration volumetric method. The combined analysis of density and viscosity data employed in this study serves as platform to understand the molecular interactions between the cholinium cation and amino acid anion in ChAAILs. In addition, the insights from these data will serve as a valuable reference in determining the most suitable cholinium amino acid-based ionic liquid (ChAAIL) for effective CO_2 capture applications.

2. Methodology

2.1 Materials

L – alanine, L – Serine, acetonitrile and methanol were used as received without undergoing purification step prior to the neutralization reaction. Acetonitrile and methanol used during washing step were of analytical grade. Both amino acids were dissolved by using ultra – pure water (18.2

MΩ.cm at 25°C) that was obtained through purification of distilled water by using Simplicity UV (Millipore). Choline hydroxide (46%, stabilized in water) was purchased from Sigma Aldrich.

2.2 Synthesis of Cholinium Amino Acid Based Ionic Liquid (ChAAIL)

Synthesis of cholinium alaninate and cholinium serinate followed a simple acid – base neutralization principle [20]. A Schott bottle containing 30 mL of choline hydroxide was cooled in a glass trough filled with ice. Although the neutralization reaction is an equimolar reaction, 10% excess of amino acid solution was used to ensure complete neutralization reaction. The amino acid solution was added to the cooled cholinium hydroxide solution in a dropwise manner under stirring condition (500 rpm) for 24 hours. Water was removed from the pure product by using rotary evaporator operated at reduced pressure and temperature of 70 mbar and 50 °C for 120 hours. Excess unreacted amino acid was removed from the pure product by washing the pure product three times with solvent mixture of acetonitrile/methanol (9:1, v/v). The precipitated amino acid crystal was filtered out of the ionic liquid. The products were further dried in vacuum oven at 50 °C at 500 mbar for 48 hours.

2.3 Cholinium Amino Acid – Based Ionic Liquid Moiety Characterization

ATR - FT-IR spectrum were generated by using PerkinElmer FT-IR equipment. Attenuated Total Reflectance (ATR) mode was used to record the IR spectra of ChAAIL at ambient condition. The analysis of the functional group presence in the amino acid based ionic liquid focused on functional group region (4000 cm^{-1} – 1400 cm^{-1}).

2.4 Thermophysical Properties Analysis

The water content of all ChAAIL were analyzed by using Karl Fisher Titrator Mettler Toledo V30 through volumetric titration. The density of each ionic liquid was studied over a temperature range from 298.15 K to 323.15 K by using a glass pycnometer. 2 mL of ionic liquid was placed into the pycnometer bottle and the pycnometer bottle was partially submerged in a water bath. The temperature of the water bath was controlled by using a thermocouple.

The dynamic viscosity of the ionic liquids was determined by using Brookfield CAP2000+ Viscometer. Due to the principal of the equipment that calculate the viscosity by using shear force, small amount of sample (67 µL) was placed on the sample plate and suitable cone spindle was placed directly on the sample. A low amount of torque was applied, and the viscosity was measured at temperature range of 298.15 K to 323.15 K.

3. Results

3.1 Characterization: ATR - FTIR

ATR - FTIR spectrum in the following Figure 1 for all ChAAIL shows the characteristic peaks absorbance of aliphatic primary amine (NH_2) as well carboxylate functional groups (COO^-). The medium peak at wavenumber region of 3350 – 3310 cm^{-1} represents N-H stretching of cholinium alaninate (3255.32 cm^{-1}) and cholinium serinate (3245.41 cm^{-1}). Strong and sharp peak of C=O stretching can also be observed in the FTIR spectrum for cholinium alaninate (1560.95 cm^{-1}) and cholinium serinate (1561.50 cm^{-1}). Apart from these two prominent peaks in the functional group region, medium peak contributed by the bending of C-H bond of methyl group can also be seen in the FT-IR spectrum of ChAAIL in the wavenumber region of 1470 cm^{-1} to 1480 cm^{-1}.

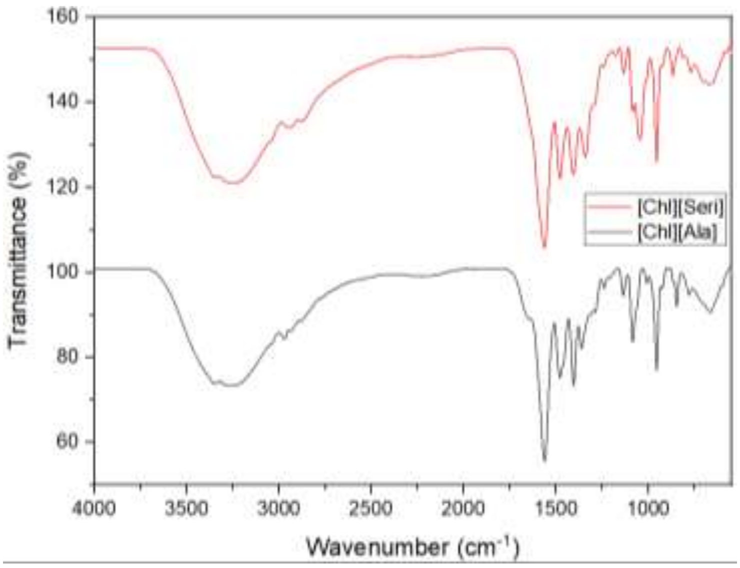

Fig. 1. ATR – FTIR of ChAAIL

3.2 Water Content

Despite an extensive drying process that includes both rotavap and vacuum oven techniques, the recorded water content for both cholinium amino acid-based ionic liquids (ChAAILs) in Table 1 remains significantly elevated, ranging from 8.67 to 10.25 wt. %. It is important to note that while the alanine anion can be considered hydrophobic due to its methyl side chain, an important observation suggests that the primary contributor to the increased water content in these synthesized ionic liquids is the cholinium cation [20]. This may be attributed to the presence of a hydroxyl functional group in the cholinium cation. The relatively high-water content observed in all ChAAILs compared to conventional ionic liquids can be mainly attributed to the hydroxyl group in the cholinium cation. Furthermore, the inherent hygroscopic nature of the amino acid anion plays a minor role in this phenomenon. Given the significant water content observed, it is essential that careful care be taken in all further drying processes to ensure that the ionic liquids are not decomposed.

Table 1
Water content of ChAAIL

ChAAIL	Water Content (wt.%)
[Chl][Ala]	8.67
[Chl][Seri]	10.25

3.3 Density and Viscosity

Both density and viscosity measurements were performed for both cholinium amino acid-based ionic liquids (ChAAILs) over a temperature range of 298.15 K to 323.15 K. The results are shown in the following Table 2 and Table 3, as both tables show the temperature dependent nature of these ionic liquids, with both density and viscosity decreasing with increasing temperature. Surprisingly, when looking at Figure 2, which plots the densities of ChAAILs versus temperature, a peculiar trend emerges, where there was huge difference between the density of [Chl][Ala] and [Chl][Seri] at all temperature points, despite the small difference in the molecular weight of [Chl][Ala] (192.26 gmol^{-1}) and [Chl][Seri] (208.26 gmol^{-1}). This intriguing finding suggests that the density of ChAAILs does not primarily depend on molecular weight or van der Waals forces. A plausible explanation for this phenomenon lies in the ability of serine anions to form hydrogen bonds. It can be concluded that the density of ChAAILs depends on the strength and prevalence of hydrogen bond interactions between the choline cation and the amino acid anions.

Table 2
Density of ChAAIL

Temperature (K)	Density, ρ (g/cm^3)	
	[Chl][Ala]	[Chl][Seri]
298.15	0.966	1.0854
303.15	0.9635	1.0828
313.15	0.9583	1.0776
323.15	0.9534	1.0721
333.15	0.9484	1.0669

Table 3
Viscosity of ChAAIL

Temperature (K)	Viscosity, η (mPa·S)	
	[Chl][Ala]	[Chl][Seri]
298.15	334.7	1051.54
303.15	203.89	595.87
313.15	77.25	199.05
323.15	27.34	73.88
333.15	12.15	31.52

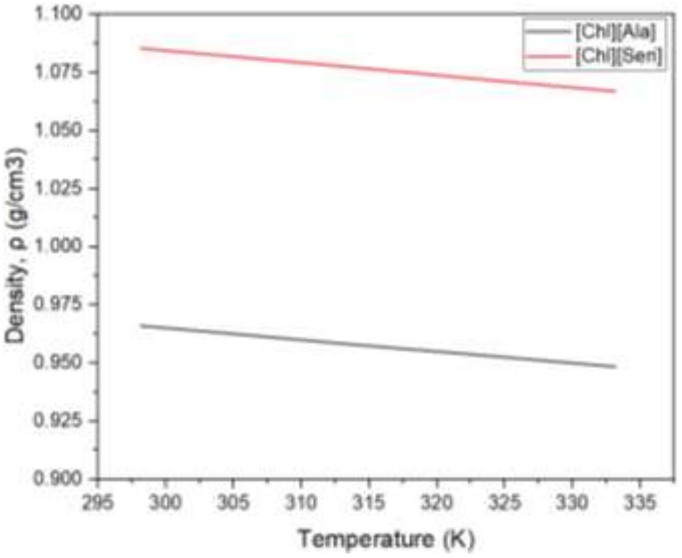

Fig. 2. Graph of ChAAIL densities against temperature

The same trend was observed in the plot of viscosities for ionic liquids based on cholinium amino acids (ChAAILs) in Figure 3 below. Compared to [Chl][Ala] that demonstrated gradual decrease in the viscosity as the temperature increased by 10 K, the viscosity of [Chl][Seri] rapidly decrease as the temperature was increased from 298.15 K to 313.15 K. The extremely high viscosity of [Chl][Seri], particularly at low temperature, was determined by the ability of serine anions to form hydrogen bond, as well as the higher molecular weight of [Chl][Seri]. Nonetheless, selecting ChAAILs with high viscosity such as [Chl][Seri] would be detrimental, as it can hinder the diffusivity of CO_2 and make it less suitable for absorption purposes. This discrepancy between density and viscosity data highlights the complex interplay of factors affecting the properties of ChAAILs and highlights the importance of considering multiple factors when developing and optimizing ionic liquids for specific applications.

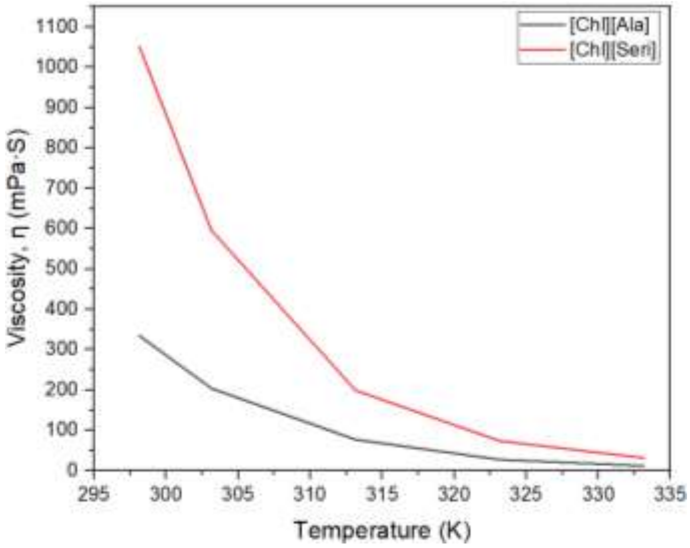

Fig. 3. Graph of ChAAIL viscosities against temperature

4. Conclusions

In summary, the comprehensive analysis of various properties, including water content, density, and viscosity, has provided a solid basis for assessing the suitability of cholinium amino acid-based ionic liquids (ChAAILs) for CO_2 absorption applications. The water content data highlighted the significant amount of moisture in the ChAAIL, while density and viscosity measurements revealed interesting relationships between the molecular composition of ChAAILs and their physical properties. Key findings included the observation that the density of ChAAILs does not solely depend on molecular weight or van der Waals forces but is influenced by the strength of the hydrogen bond interactions between the choline cation and the amino acid anions. On the other hand, the viscosity showed a clear correlation with the molecular weight of the anion, indicating the influence of intermolecular forces, especially van der Waals forces. Nevertheless, further research and optimization are required to fully exploit the potential of ChAAILs in CO_2 capture processes and ensure their practicality and efficiency in real-world applications.

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