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Thermophysical Properties and CO_2 Absorption of Ammonium-Based Protic Ionic Liquids Containing Acetate and Butyrate Anions

Normawati M. Yunus [1,*], Nur Hamizah Halim [2], Cecilia Devi Wilfred [1], Thanabalan Murugesan [3], Jun Wei Lim [2] and Pau Loke Show [4]

1 Department of Fundamental and Applied Sciences, Center of Research in Ionic Liquids (CORIL), Institute of Contaminant Management for Oil and Gas, Universiti Teknologi PETRONAS, Seri Iskandar 32610, Perak, Malaysia
2 Department of Fundamental and Applied Sciences, Universiti Teknologi PETRONAS, Seri Iskandar 32610, Perak, Malaysia
3 Department of Chemical Engineering, Universiti Teknologi PETRONAS, Seri Iskandar 32610, Perak, Malaysia
4 Department of Chemical and Environmental Engineering, Faculty of Science and Engineering, University of Nottingham Malaysia, Jalan Broga Semenyih 43500, Selangor, Malaysia
* Correspondence: normaw@utp.edu.my; Tel.: +605-368-7689; Fax: +605-365-5905

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Abstract: Ionic liquids, which are classified as new solvents, have been identified to be potential solvents in the application of CO_2 capture. In this work, six ammonium-based protic ionic liquids, containing ethanolammonium [EtOHA], tributylammonium [TBA], bis(2-ethylhexyl)ammonium [BEHA] cations, and acetate [AC] and butyrate [BA] anions, were synthesized and characterized. The thermophysical properties of the ammonium-based protic ionic liquids were measured. Density, ρ, and dynamic viscosity, η, were determined at temperatures between 293.15 K and 363.15 K. The density and viscosity values were correlated using empirical correlations and the thermal coefficient expansion, α_p, and molecular volume, V_m, were estimated using density values. The thermal stability of the ammonium-based protic ionic liquids was investigated using thermogravimetric analyzer (TGA) at a heating rate of 10 °C·min^{-1}. The CO_2 absorption of the ammonium-based ionic liquids were measured up to 20 bar at 298.15 K. From the experimental results, [BEHA][BA] had the highest affinity towards CO_2 with the mol fraction of CO_2 absorbed approaching 0.5 at 20 bar. Generally, ionic liquids with butyrate anions have better CO_2 absorption than that of acetate anions while [BEHA] ionic liquids have higher affinity towards CO_2 followed by [TBA] and [EtOHA] ionic liquids.

Keywords: ammonium-based protic ionic liquids; density; thermal expansion coefficient; viscosity; thermal stability; CO_2 absorption

1. Introduction

Natural gas consists mainly of methane as well as other higher alkanes in varied amounts. It is mainly used as a fuel and as a raw material in petrochemical industries [1]. While natural gas is principally a mixture of combustible hydrocarbons, many natural gases also contain impurities, such as carbon dioxide, CO_2, hydrogen sulfide, H_2S, and water. Refining processes are required to remove all of these unwanted impurities from natural gas. Besides water and higher-molecular-weight hydrocarbons, one of the most crucial parts of gas processing is the elimination of CO_2 and this process is normally done by means of chemical absorption techniques using alkanolamine solutions. Despite the successful practice of using alkanolamines for CO_2 removal, several disadvantages have

been identified, such as solvent loss and degradation as well as corrosion issues [2]. In view of these issues, there is a need to develop new alternative, yet effective solvents for the same purposes. Ionic liquids have emerged as new solvents that have potential to be used for CO_2 removal due to their special features, namely non-detectable vapor pressure, wide liquid range, and remarkable thermal stability. Ionic liquids are low melting salts with typical melting points of below 100 °C. Furthermore, there are countless possible combinations of cations and anions that can yield ionic liquids and this flexibility is utilized to design ionic liquids based on the application. Ionic liquids are used in many applications, such as in chemical reactions and separation processes [3–6]. In the field of CO_2 capture using ionic liquids, initial work on the CO_2-ionic liquid system was done in 2001 [7] and, following this discovery, extensive works have been done to explore the absorption of CO_2 in ionic liquids under various operating conditions [8–15]. Imidazolium-based ionic liquids were used in most of the study of CO_2 absorption. They are highly unsymmetrical and therefore have low melting points. Recently, protic ionic liquids have been used in the study of CO_2 capture [16,17]. Protic ionic liquids are formed by a proton transfer between an equimolar amount of a Brønsted acid and a Brønsted base. The modern type of protic ionic liquids have been described by Ohno and co-workers [18] and an extensive review on the properties and applications of protic ionic liquids has been provided by Greaves and Drummond [19] who also noted the ability of protic ionic liquids to support amphiphile self-assembly [20,21]. The interest in the ionicity of protic ionic liquids has come to light due to the unlikeliness of complete proton transfer between the acid and base contributing to the presence of a neutral acid and base mixture [19,22,23]. MacFarlane and Seddon [24] proposed a limit of a 1% neutral species presence in an ionic liquid to be called 'pure ionic liquid'. The term pseudo-protic ionic liquid was suggested by Doi et al. [25] after they discovered that a mixture of *N*-methylimidazole and acetic acid exhibited electrical conductivity behavior even though the mixture was mostly dominated by neutral species rather than ions when inspected using Raman spectroscopy.

Nevertheless, the simple synthesis pathway of protic ionic liquids, i.e., a one-step neutralization reaction, and their proven ability to absorb CO_2 motivated us to explore this type of ionic liquids in the field of CO_2 capture. Nonetheless, physical properties, such as density, viscosity, and thermal stability of ionic liquids, are very important prior to using these new solvents in any applications. Precise understanding on the thermophysical properties is important as it is required to evaluate the suitability of ionic liquids to be used at an industrial scale [26]. For instance, viscosity is an important property for the design of industrial processes involving heat and mass transfer and dissolution of compounds in fluids [27]. Therefore, the aim of our work was to synthesize several new ammonium-based protic ionic liquids using a 1-step neutralization reaction, measure their thermophysical properties, and, lastly, test their ability to capture CO_2. In this work, six ammonium-based protic ionic liquids, containing acetate and butyrate anions, were synthesized using solvent-free, 1-step neutralization reaction. The density, dynamic viscosity, and thermal stability of these ionic liquids were determined. The density values enable the estimation of thermal expansion coefficient and the molecular volume of the ionic liquids. To assess the capability of these ionic liquids towards CO_2, absorption of CO_2 was done using a solubility cell and the screening was done in the CO_2 pressure range up to 20 bar and at 298.15 K. Results showed that the ammonium-based protic ionic liquids synthesized in this study have the potential to absorb CO_2.

2. Materials and Methods

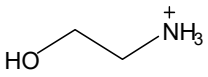
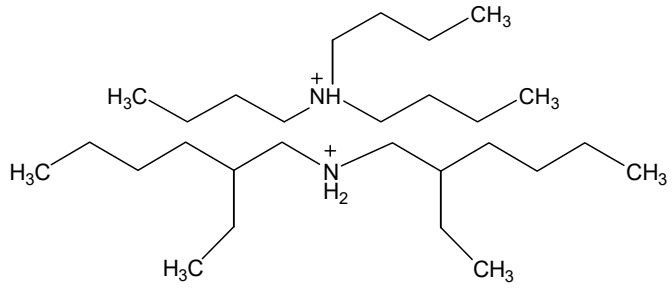
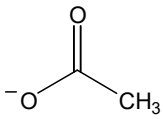
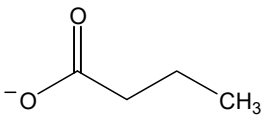
2.1. Chemicals

Three amines and two organic acids from Merck Sdn. Bhd. were used in the production of the ammonium-based protic ionic liquids. All chemicals were of analytical grade. The amines and acids CAS numbers, abbreviations, and grades are as follows: ethanolamine (141–43–5, 99%), bis(2–ethylhexyl)amine (106–20–7, 99%), tributylamine (102–82–9, 99%), acetic acid (64–19–7, 99.8%), and butyric acid (107–92–6, 99%).

2.2. Synthesis

For the synthesis of each of the ammonium-based protic ionic liquids, an equimolar amount of the acid was added dropwise to the amine at ambient conditions and the mixture was consistently stirred for 24 h to facilitate mixing. The resulting solution was dried under vacuum at 65 °C for 6 h to remove remaining reactants. The final product was kept in a seal container until further use. The combinations of two acids and three amines produce six ammonium-based protic ionic liquids. Table 1 shows the structures and the abbreviation used for the ionic liquids. All ionic liquids exist as liquids except [BEHA][AC], which exists as a solid compound at room temperature.

Table 1. Structures of cations and anions, names and abbreviations.

Structure	Name and Abbreviation
	Ethanolammonium, [EtOHA]
	Tributylammonium, [TBA]
	Bis(2-ethylhexyl)ammonium, [BEHA]
	Acetate, [AC]
	Butyrate, [BA]

2.3. NMR and Water Content

The structure of the ammonium-based protic ionic liquids was analyzed and confirmed via nuclear magnetic resonance (NMR) spectroscopy. About 5 mg sample of ionic liquid was dissolved in 6 mL deuterated solvent and the sample's purity was determined using 500 MHz Bruker NMR Oxford Instrument. Coulometric Karl Fischer autotitrator DL39 from Mettler was used to determine the water content of the ionic liquids.

2.4. Thermophysical Characterization

The viscosity and density of the ammonium-based protic ionic liquids were determined simultaneously using Anton Parr Stabinger Viscometer SVM3000 in the temperature range of 293.15 K to 363.15 K. The temperature measurement's accuracy was within 0.02 K while the reproducibility of the viscosity and density measurements were 0.35% and $\pm 5.10^{-4}$ g·cm^{-3}, respectively [28]. The decomposition temperatures of the ionic liquids were examined by means of thermogravimetric analyzer, TGA Perkin Elmer STA 6000. About 10 mg of sample was loaded into a platinum pan and the sample was heated at a heating rate of 10 °C·min^{-1} under nitrogen flow.

2.5. CO_2 Absorption Measurement

The ability of the ammonium-based protic ionic liquids to absorb CO_2 was investigated based on a pressure drop technique using a solubility cell as described in our previous publication [29]. The

solubility cell consists of an equilibrium cell and a gas vessel immersed in a thermostatic bath. In a pressure drop method, the gas with a known pressure at constant volume is allowed to be in contact with the ionic liquid in the equilibrium cell and the pressure drop is monitored as the gas absorbs into the ionic liquid until equilibrium is attained. In a typical experiment, the equilibrium cell was loaded with a pre-weighed amount of the ionic liquid and the equilibrium cell was evacuated to remove any gases. In the gas vessel, CO_2 was allowed to stabilize before being quickly charged into the equilibrium cell. The CO_2-ionic liquid system was assumed to achieve equilibrium when the pressure attained a constant value. The system was maintained in that conditions for an additional two hours to ensure equilibration. Equation (1) was used to calculate the amount of CO_2 absorbed in the ionic liquid, n_2 [30]:

$$n_2 = \frac{P_{ini}V_{total}}{Z_2(P_{ini}, T_{ini})RT_{ini}} - \frac{P_{eq}\left[V_{total} - V_{liq}\right]}{Z_2(P_{eq}, T_{eq})RT_{eq}}, \quad (1)$$

where P_{ini} and T_{ini} are the initial pressure and temperature of the system, P_{eq} and T_{eq} are the pressure and temperature of the system at equilibrium, V_{total} is the volume of the equilibrium cell, V_{liq} is the volume of ionic liquid, R is the gas constant, and Z_2 represents the compressibility factor of the gas. Z_2 can be calculated using Soave–Redlich–Kwong equation of state [31]. The mole fraction of CO_2 absorbed in the ionic liquid (x_2) was calculated using Equation (2):

$$x_2 = \frac{{n_2}^{liq}}{\left({n_2}^{liq} + {n_1}^{liq}\right)}, \quad (2)$$

where ${n_2}^{liq}$ represents the mole of dissolved CO_2 and ${n_1}^{liq}$ is the mole of the ionic liquid.

3. Results and Discussion

In this work, six ammonium-based protic ionic liquids—ethanolammonium acetate [EtOHA][AC], ethanolammonium butyrate [EtOHA][BA], tributylammonium acetate [TBA][AC], tributylammonium butyrate [TBA][BA], bis(2-ethylhexyl)ammonium acetate [BEHA][AC], and bis(2-ethylhexyl)ammonium butyrate [BEHA][BA]—were synthesized and characterized. All the ammonium-based protic ionic liquids exist as liquids at room temperature except [BEHA][AC], which is a solid. The NMR and water content of each ionic liquids are presented as follows:

[EtOHA][AC]: ^{1}H NMR (500 MHz, D_2O): δ 3.613 [t, 2H, H_2(-OH)], 2.922 [t, 2H, CH_2(-NH_2)], 1.726 [s, 3H, CH_3]. Water content: 2.93%
[EtOHA][BA]: ^{1}H NMR (500 MHz, D_2O): δ 3.669 [t, 2H, CH_2(-OH)], 2.988 [t, 2H, CH_2(-NH_2)], 2.010 [t, 2H, CH_2(-COOH)], 1.375–1.448 [m, 2H, CH_2], 0.747 [t, 3H, CH_3]. Water content: 2.06%
[BEHA][AC]: ^{1}H NMR (500 MHz, D_2O): δ 2.861 [d, 4H, CH_2(-NH)], 1.805 [s, 3H, CH_3], 1.613–1.677 [m, 2H, CH], 1.181–1.309 [m, 16H, CH_2], 0.786 [t, 12H, CH_3]. Solid
[BEHA][BA]: ^{1}H NMR (500 MHz, D_2O): δ 2.856 [d, 4H, CH_2(-NH)], 2.062 [t, 2H, CH_2(-COOH)], 1.582–1.660 [m, 2H, CH], 1.412–1.486 [m, 2H, CH_2(AC)], 1.236–1.339 [m, 16H, CH_2], 1.214-1.229 [t,t 15H, CH_3]. Water content: 0.15%
[TBA][AC]: ^{1}H NMR (500 MHz, D_2O): δ 3.002 [t, 4H, CH_2(-NH)], 1.788 [s, 3H, CH_3], 1.508–10571 [m, 6H, CH_2], 1.207–1.282 [m, 6H, CH_2], 0.805 [t, 9H, CH_3]. Water content: 0.47%
[TBA][BA]: ^{1}H NMR (500 MHz, D_2O): δ 3.003 [t, 6H, CH_2(-NH)], 2.031 [t, 2H, CH_2(-COOH)], 1.510–1.573 [m, 6H, CH_2], 1.394–1.468 [m, 2H, CH_2(AC)], 1.211-1.285 [m, 6H, CH_2], 0.809 [t, 9H, CH_3], 0.768 [t, 3H, CH_3(AC)]. Water content: 0.23%

3.1. Thermophysical Properties

The experimental density and dynamic viscosity values for all liquid samples of synthesized ammonium-based protic ionic liquids are presented in Tables 2 and 3. The experimental densities of [EtOHA][AC], [EtOHA][BA], [BEHA][BA], [TBA][AC], and [TBA][BA] as a function of temperature

are shown in Figures 1–3. [BEHA][AC] is not included as it exists as solid. As can be seen from Figure 1, the density of all five ammonium-based protic ionic liquids decreased gradually and linearly with increasing temperature over the range of temperature studied. An increase in temperature caused higher mobility of the ions which, in turn, weakens the intermolecular forces between the constituent ions and correspondingly increases the unit volume for these ions [32]. The density of these ammonium-based protic ionic liquids was slightly affected by the length of the alkyl chain of the anion in which the density of ionic liquids with the [AC] anion was higher than of ionic liquids with the [BA] anion for a fixed cation, as shown in Figure 2a,b. This observation is consistent with the literature in which it has been shown that the density value drops as the alkyl chain gets longer [28,32–37]. Our experimental density value of [EtOHA][AC] is in good agreement with Kurnia et al. [35] and Hosseini et al. [38] with the value differences of less than 0.2% and 0.8%, respectively. Generally, effective arrangement of ions in a liquid can increase the density of the liquid due to a greater number of ions available in a unit volume [39]. Based on our experimental results, as shown in Figure 3, ionic liquids with the [EtOHA] cation have higher density values compared to the rest, suggesting a better packing of the ions due to the small size of the cation. [TBA][BA] had the lowest density values at all temperatures due to the combined effects of branching of the cation, which increases the asymmetricity and steric hindrance of the ionic liquid [32], along with the large size of the alkyl chain of the [BA] anion.

Table 2. Density (ρ) values of ionic liquids from 293.15 K to 363.15 K.

T/K	ρ (g·cm^{-3})				
	[EtOHA][AC]	[EtOHA][BA]	[BEHA][BA]	[TBA][AC]	[TBA] [BA]
293.15	1.1468	1.0772	0.8695	0.9118	0.8591
303.15	1.1410	1.0725	0.8613	0.9035	0.8531
313.15	1.1359	1.0657	0.8532	0.8952	0.8445
323.15	1.1305	1.0579	0.8451	0.8869	0.8356
333.15	1.1250	1.0516	0.8368	0.8785	0.8268
343.15	1.1194	1.0452	0.8285	0.8700	0.8185
353.15	1.1137	1.0387	0.8203	0.8614	0.8102
363.15	1.1079	1.0324	0.8124	0.8527	0.8020

Table 3. Dynamic viscosity (η) values of ionic liquids from 293.15 K to 363.15 K.

T/K	η (mPa·s)				
	[EtOHA][AC]	[EtOHA][BA]	[BEHA][BA]	[TBA][AC]	[TBA] [BA]
293.15	385.760	1814.000	26.061	1.8482	8.368
303.15	197.860	883.310	15.364	1.5090	5.832
313.15	110.780	464.320	9.780	1.1485	4.225
323.15	66.947	261.220	6.628	1.0573	3.185
333.15	43.099	155.690	4.706	0.9041	2.457
343.15	29.214	97.348	3.478	0.7886	1.949
353.15	20.677	63.345	2.652	0.6928	1.579
363.15	15.157	42.651	1.874	0.6149	1.287

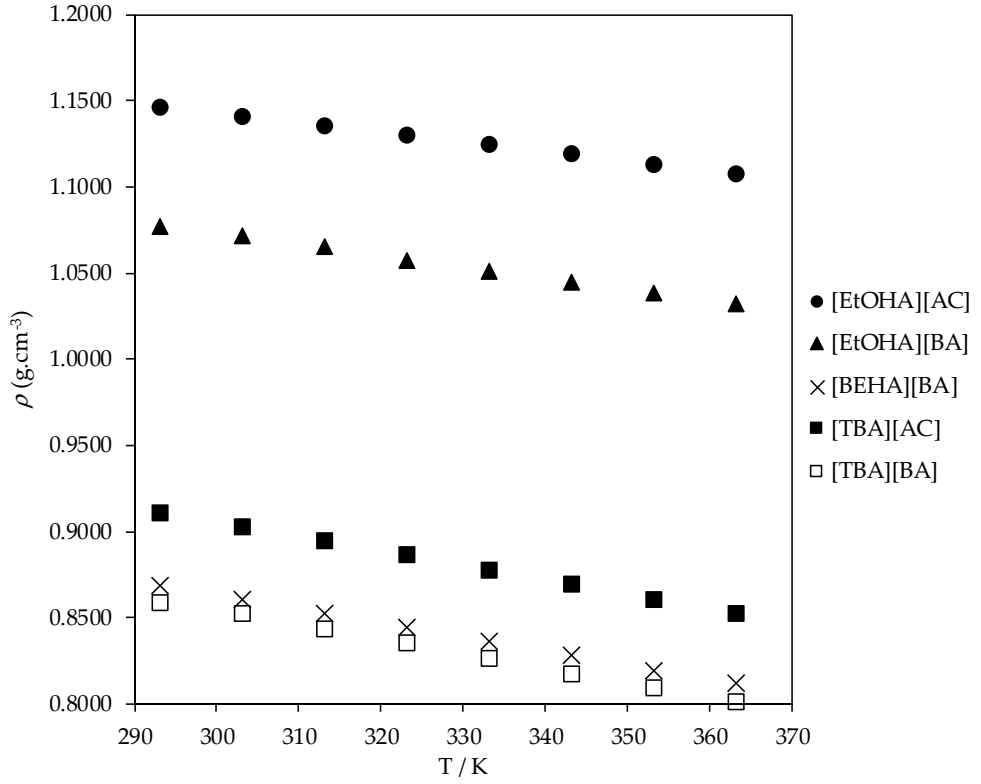


Figure 1. Plot of experimental density (ρ) values of ammonium-based protic ionic liquids.

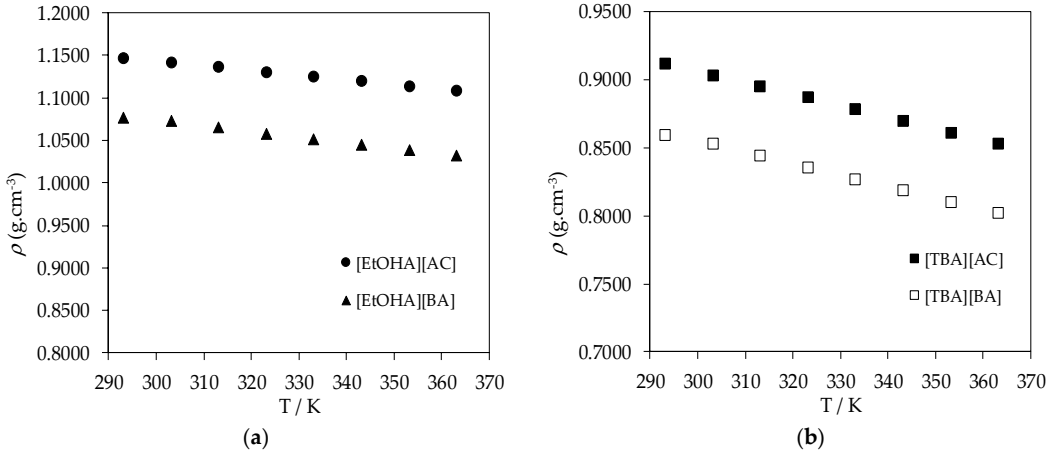


Figure 2. (**a**) Plot of experimental density (ρ) values of [EtOHA][AC] and [EtOHA][BA] and (**b**) plot of experimental density (ρ) values of [TBA][AC] and [TBA][BA] as a function of temperature.

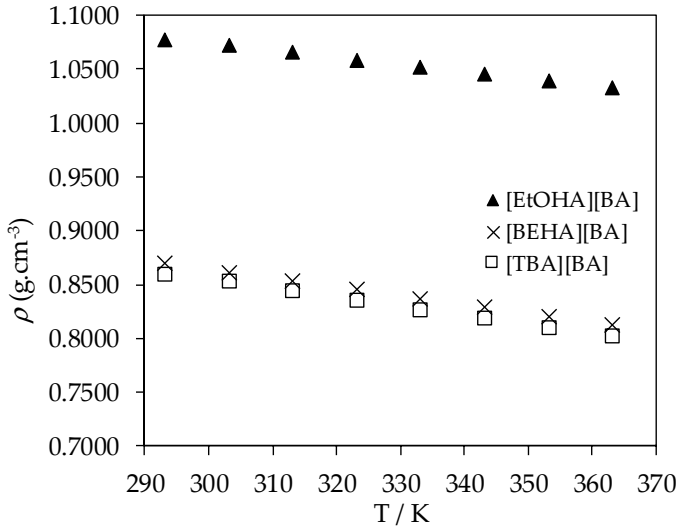
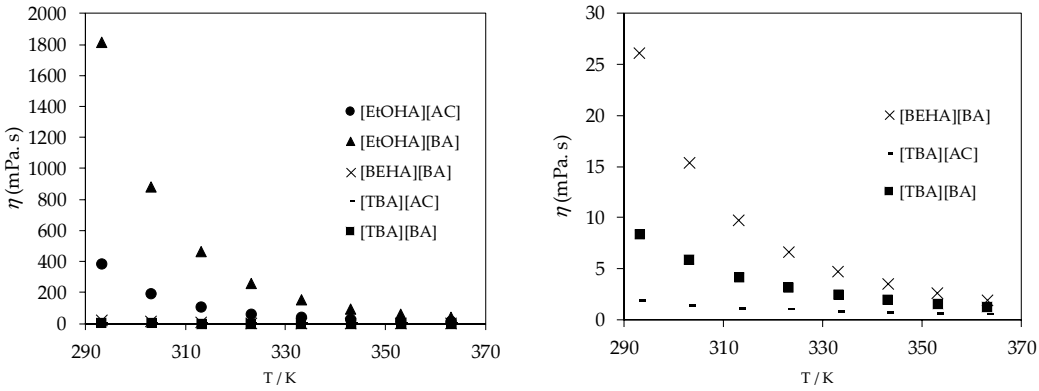


Figure 3. Plot of experimental density (ρ) values of [EtOHA][BA], [BEHA][BA], and [TBA][BA] as a function of temperature.

The dynamic viscosity of the ammonium-based protic ionic liquids, presented in Figure 4, dropped significantly as the temperature increased and the viscosity of ionic liquids with a [BA] anion was higher than that of ionic liquids with an [AC] anion for each type of cation studied in this work, as shown in Figure 5. The longer the alkyl chain in the ionic liquid structure, the higher the viscosity of the ionic liquids due to the increase in van der Waals attraction between the aliphatic alkyl chains [35]. On the other hand, [EtOHA] ionic liquids have remarkable high viscosity values compared to [BEHA] and [TBA] ionic liquids due to the presence of the hydroxyl group which enables a hydrogen bonding interaction between the structures of the ions.



(**a**) (**b**)

Figure 4. (**a**) Plot of experimental viscosity (η) values of ammonium based ionic liquids and (**b**) plot of experimental viscosity (η) values of [BEHA][BA], [TBA][AC], and [TBA][BA].

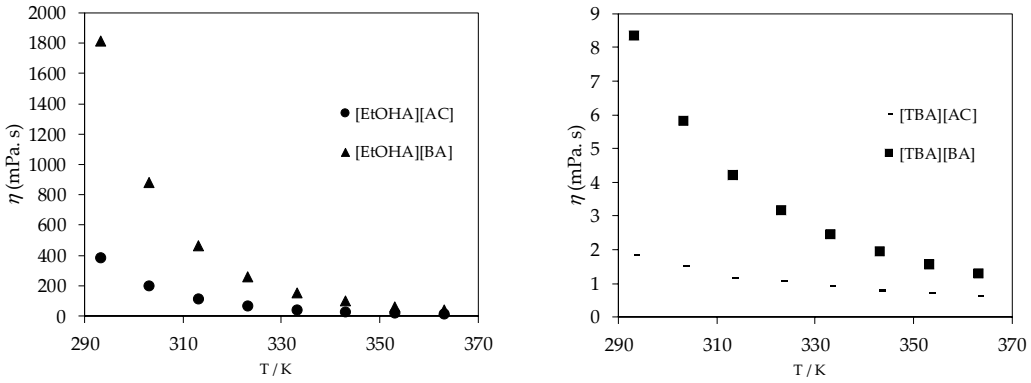


Figure 5. (**a**) plot of experimental viscosity (η) values of [EtOHA][AC] and [EtOHA][BA] ionic liquids and (**b**) plot of experimental viscosity (η) values of [TBA][AC] and [TBA][BA].

The values of density, ρ and dynamic viscosity, η were fitted using Equations (3) and (4) [28]:

$$\rho = A_0 + A_1 T, \tag{3}$$

$$\lg \eta = A_2 + A_3/T, \tag{4}$$

where ρ is the density, η is the dynamic viscosity of the ionic liquids, T is temperature in K, and A_0, A_1, A_2, and A_3 are correlation coefficients determined using the method of least squares. The calculated correlation coefficients together with standard deviations, SD are presented in Tables 4 and 5. The standard deviations, SD, were calculated using Equation (5) in which Z_{expt} and Z_{calc} are experimental and calculated values, respectively, while n_{DAT} is the number of experimental points:

$$SD = \sqrt{\frac{\sum_{i}^{n_{DAT}} (Z_{\exp t} - Z_{calc})^2}{n_{DAT}}}. \tag{5}$$

Table 4. Fitting parameters of Equation (3) for density (ρ) correlation and standard deviation (SD) from Equation (5).

Ionic Liquid	A_0	A_1	SD
[EtOHA][AC]	1.3087	−0.0006	0.016
[EtOHA][BA]	1.2702	−0.0007	0.015
[BEHA][BA]	1.1093	−0.0008	0.006
[TBA][AC]	1.1592	−0.0008	0.014
[TBA][BA]	1.1051	−0.0008	0.011

Table 5. Fitting parameters of Equation (4) for dynamic viscosity (η) correlation and standard deviation (SD) from Equation (5).

Ionic Liquid	A_2	A_3	SD
[EtOHA][AC]	−4.7222	2127.7	0.031
[EtOHA][BA]	−5.1998	2469.4	0.021
[BEHA][BA]	−4.4045	1696.4	0.020
[TBA][AC]	−2.1829	713.31	0.014
[TBA][BA]	−3.2888	1229.3	0.011

The thermal expansion coefficient, α_p, for the ammonium-based protic ionic liquids can be calculated using Equation (6) [28] while the molecular volume, V_m can be estimated from Equation (7) in which M is the molar mass of the ionic liquid and N_A represents the Avogadro's number [32,36,37]:

$$\alpha_p = -1/\rho \cdot (\partial\rho/\partial T)_p = -(A_1)/(A_0 + A_1 T) \text{ and} \quad (6)$$

$$V_m = M/N_A \cdot \rho. \quad (7)$$

The calculated thermal expansion coefficients and molecular volume values of the ammonium-based protic ionic liquids are presented in Tables 6 and 7. The calculated values lie in the range of (5.3 to 9.8)·10^{-4} K^{-1} for all five ionic liquids. The thermal expansion coefficients were found to be quite consistent over the temperature range studied and therefore are considered to be temperature independent. The pattern of the results is consistent with other types of ionic liquids [27,28,36,40,41]. The molecular volume, V_m, of the [BA] ionic liquid was greater than that of [AC] for a fixed cation and this may be attributed to the presence of additional CH_2 groups [36,37]. In this work, the V_m decreased in the sequence of [BEHA] > [TBA] > [EtOHA] for a fixed anion, i.e., [BA].

Table 6. Thermal expansion coefficients (α_p) of the ionic liquids calculated using Equation (6).

T/K	$\alpha_p \times 10^{-4}/(K^{-1})$				
	[EtOHA][AC]	**[EtOHA][BA]**	**[BEHA][BA]**	**[TBA][AC]**	**[TBA] [BA]**
293.15	5.3	6.6	9.1	8.7	9.2
303.15	5.3	6.6	9.2	8.7	9.3
313.15	5.4	6.7	9.3	8.8	9.4
323.15	5.4	6.7	9.4	8.9	9.4
333.15	5.4	6.8	9.5	9.0	9.5
343.15	5.4	6.8	9.6	9.0	9.6
353.15	5.5	6.8	9.7	9.1	9.7
363.15	5.5	6.9	9.8	9.2	9.8

Table 7. Molecular volume (V_m) of the ionic liquids calculated using Equation (7).

T/K	nm^3				
	[EtOHA][AC]	**[EtOHA][BA]**	**[BEHA][BA]**	**[TBA][AC]**	**[TBA] [BA]**
293.15	0.1754	0.2300	0.6295	0.4470	0.5287
303.15	0.1763	0.2310	0.6355	0.4511	0.5324
313.15	0.1771	0.2325	0.6416	0.4553	0.5378
323.15	0.1780	0.2342	0.6477	0.4596	0.5436
333.15	0.1788	0.2356	0.6542	0.4640	0.5493
343.15	0.1797	0.2371	0.6607	0.4685	0.5549
353.15	0.1807	0.2386	0.6673	0.4732	0.5606
363.15	0.1816	0.2400	0.6738	0.4780	0.5663

The thermal decomposition (T_d) of the ammonium-based protic ionic liquids were measured at a heating rate of 10 °C·min^{-1}. The T_d was approximately determined by the intersection of the baseline weight from the beginning of the measurement and the tangent of the weight against the temperature curve as the decomposition process occurs. The T_d of the ionic liquids are presented in Table 8 and the thermal decomposition curves for [EtOHA][BA] and [BEHA][BA] are given in Figure 6. The thermal stability of the ammonium-based protic ionic liquids in this study varied with the ion combination. The T_d of [BA] ionic liquid was higher than that of [AC] ionic liquid for every type of cation studied while [EtOHA] ionic liquids displayed the highest T_d followed by [BEHA] and [TBA]. However, ammonium-based protic ionic liquids in this work and from the literature [36] tend to possess lower thermal stability compared to other ionic liquids, such as imidazolium and pyridinium

ionic liquids [28,41,42]. However, generalization must not be made as the thermal stability depends largely on the combination of the cation and anion of the ionic liquids.

Table 8. Thermal decomposition (T_d) temperature of the ionic liquids.

	[EtOHA][AC]	[EtOHA][BA]	[BEHA][AC]	[BEHA][BA]	[TBA][AC]	[TBA] [BA]
T/°C	147.23	237.47	124.89	146.06	111.46	120.58

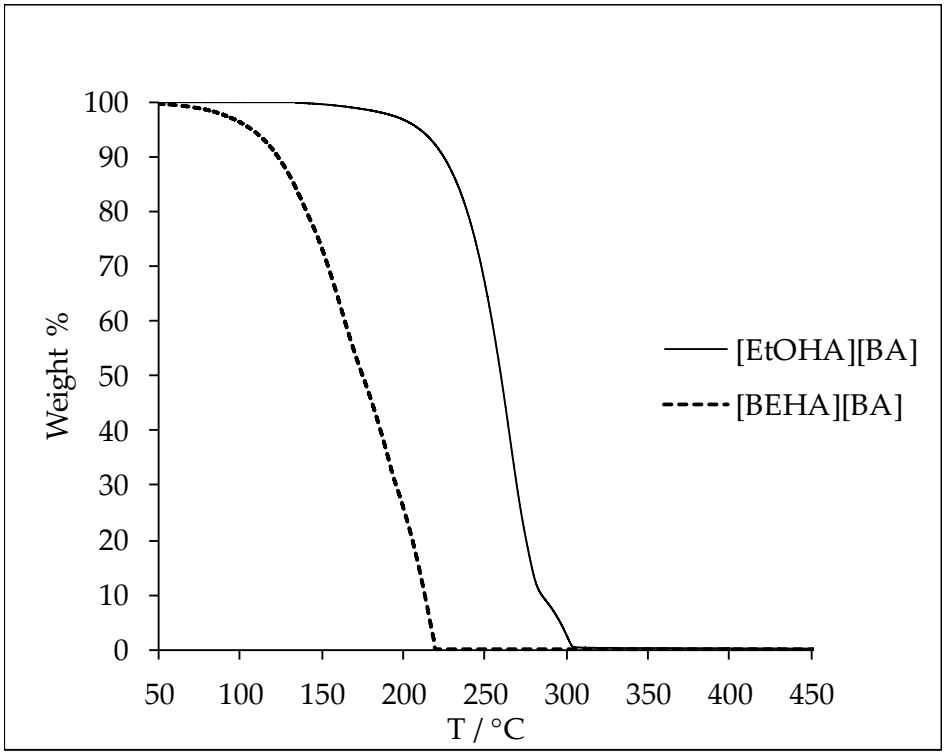


Figure 6. Plot of thermal decomposition of [EtOHA][BA] and [BEHA][BA].

3.2. CO_2 Absorption

The experimental results of CO_2 absorption in the ammonium-based protic ionic liquids are shown in Figure 7. Generally, the CO_2 absorption in these ammonium-based protic ionic liquids increased with pressure following Henry's law; the solubility of a gas in a liquid is proportional to the partial pressure of the gas above the surface of the liquid. The mol fraction of CO_2 absorbed in the ammonium-based protic ionic liquids was in the range of about 0.02 to 0.48 and up to 20 bar at 298.15 K. The effects of cation structure on the CO_2 absorption in the ionic liquids are shown in Figure 8. For a fixed anion, the solubility of CO_2 increased in the sequence of [EtOHA] < [TBA] < [BEHA] where the mol fraction of CO_2 absorbed in [BEHA][BA] was 0.486 in comparison to 0.328 and 0.307 in [TBA][BA] and [EtOHA][BA], respectively. Meanwhile, Figure 9 indicates a slight increase in the CO_2 solubility when the anion of a common cation was changed from [AC] to [BA]. Based on our experimental results, there is a relationship between absorption of CO_2 with the density and the molecular volume of the ionic liquids. As the density decreases and molecular volume increases, the fractional free volume increases and, thus, the solubility of CO_2 increases [43,44]. By using a common anion, the CO_2 absorption in [BEHA][AC] was compared with 1-ethyl-3-methylimidazolium acetate, [EMIM][AC] [45] and 1-butyl-3-methylimidazolium acetate, [BMIM][AC] [11]. At about 20 bar and 298.15 K, there was only a marginal difference between the CO_2 solubility in [BEHA][AC] compared to that of [EMIM][AC] and [BMIM][AC]. This result shows a positive indication that our newly synthesized [BEHA][AC] and [BEHA][BA] ionic liquids have comparable performance towards CO_2 capture when compared to

more established type of ionic liquids. However, more experimental investigation and data are needed to further evaluate the potential ability of our ammonium-based protic ionic liquids in the application of CO_2 capture.

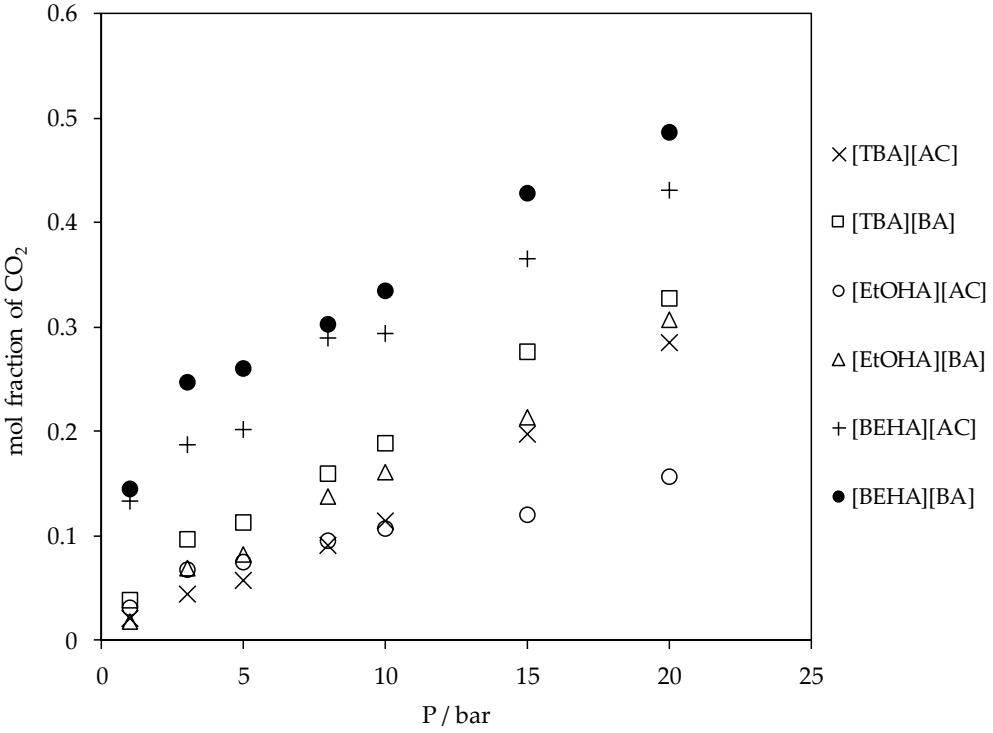


Figure 7. Plot of CO_2 absorption in ammonium-based protic ionic liquids at 298.15 K.

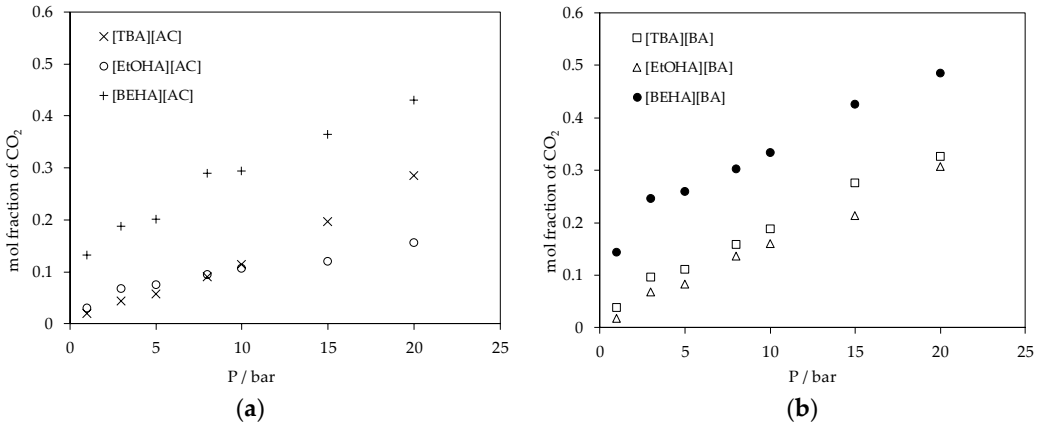


Figure 8. (**a**) Plot of CO_2 absorption in ammonium-based protic ionic liquids with [AC] anion and (**b**) plot of CO_2 absorption in ammonium-based protic ionic liquids with [BA] anion at 298.15 K.

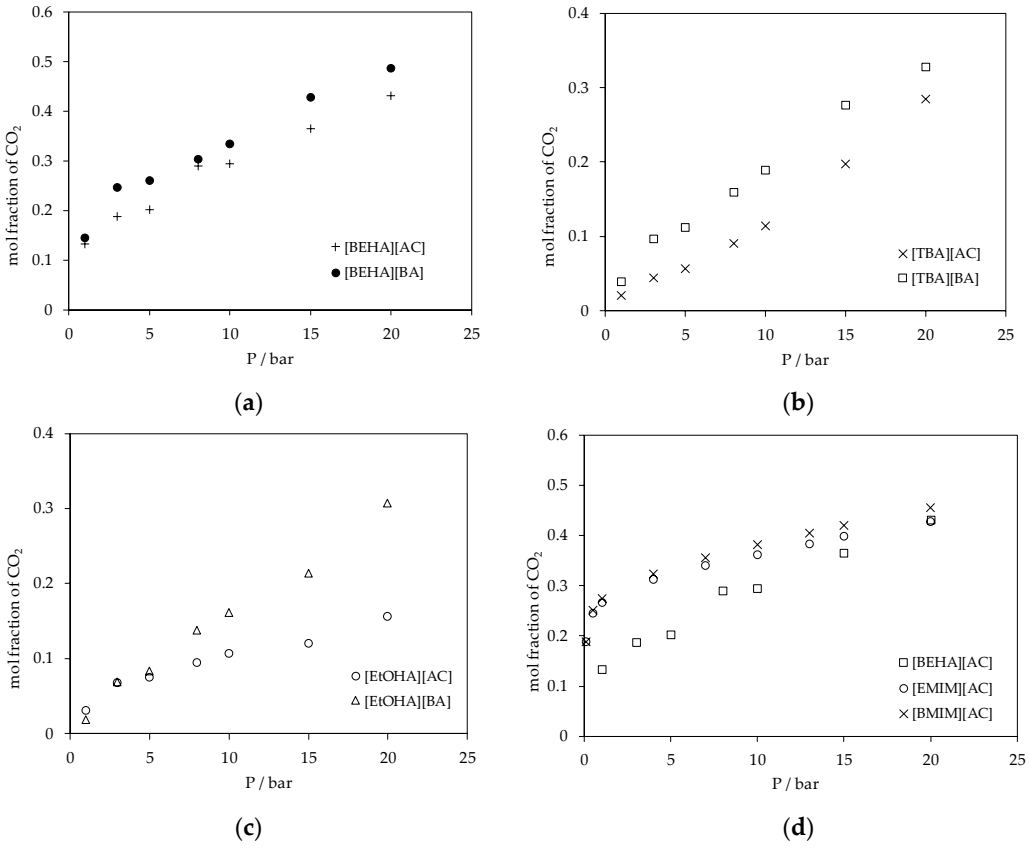


Figure 9. (**a**) Plot of CO_2 absorption in ammonium-based protic ionic liquids with the [BEHA] cation; (**b**) plot of CO_2 absorption in ammonium-based protic ionic liquids with the [TBA] cation; (**c**) plot of CO_2 absorption in ammonium-based protic ionic liquids with the [EtOHA] cation and; and (**d**) plot of CO_2 absorption in [BEHA][AC], [EMIM][AC] [45] and [BMIM][AC] [11] at 298.15 K.

4. Conclusions

Six ammonium-based protic ionic liquids were successfully synthesized via solvent-free 1-step neutralization reaction. The density, viscosity, and decomposition temperature were measured. The thermal expansion coefficient and the molecular volume were calculated using the density values. The density and viscosity values were inversely proportional with temperature in the range of temperature studied at atmospheric pressure. The density decreased when the alkyl chain of the anion increased, while the viscosity increased with the alkyl chain of the anion. The decomposition temperature of the ammonium-based protic ionic liquids was affected by the combination of cation and anion and [EtOHA] ionic liquids had the highest thermal stability when compared to the other ionic liquids. The absorption of CO_2 in the six ammonium-based protic ionic liquids was measured at 298.15 K and up to a pressure of 20 bar. The CO_2 absorption values in the ammonium-based protic ionic liquids increased with pressure and both the cation and anion affected the solubility of CO_2 in the ionic liquids. The amount of CO_2 absorbed was affected by the length of the alkyl chain of the anion while [BEHA] ionic liquids displayed higher CO_2 absorption capacity compared to [TBA] and [EtOHA] ionic liquids. Results indicate the potential of the ammonium-based protic ionic liquids to be used as solvents for CO_2 capture.

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