Chemical Sciences Journal

Losetty et al., Chem Sci J 2016, 7:2
DOI: 10.4172/2150-3494.1000128

Research Article Open Access

Recent Advances and Thermophysical Properties of Acetate-based Protic Ionic Liquids

Venkatramana Losetty[1], **Magaret Sivapragasam**[1] **and Cecilia Devi AP Wilfred**[1,2]*

[1]*Center of Research in Ionic Liquids (CORIL), Universiti Teknologi PETRONAS, Bandar Seri Iskandar, Perak 32610, Malaysia*
[2]*Faculty of Fundamental and Applied Science, Universiti Teknologi PETRONAS, 32610, Tronoh, Perak, Malaysia*

Abstract

Protic Ionic Liquids (PILs), a substantial branch of the infamous Ionic Liquids (ILs) have gained much attention in recent years. They have been the “go-to” solvent of choice in many areas such as chromatography, catalysis, fuel cells, biological applications etc., due to their thermophysical properties and their ability to be tunable based on task specificity. This review covers two parts, namely; a brief description on the thermophysical properties of acetate PILs (density, speed of sound, viscosity and decomposition temperature) and its current applications in the industry. The collation of the physicochemical data consents structure-property trends would be discussed, and these can be used as a foundation for the development of new PILs to achieve specific properties. Economically, PILs have been suggested as “greener” alternatives to conventional solvents in various industrial applications hence, in order to assess their suitability for such purposes, a thorough evaluation of their mutagenicity, toxicity and carcinogenicity is crucial.

Keywords: Protic ionic liquid; Thermophysical property; Acetate ionic liquids

Introduction

Ionic Liquids (ILs) are molten salt consisting entirely of ions that can be paired up by an enormous number of cations and anions. Such examples include anions- halides, phosphates, sulphates, borates, acetates and cations- bulky dissymmetrical long/short alkyl chained (such as trialkylphosphonium, trialkylammonium, imidazolium, pyridinium) [1-3]. Since it can be made up from unlimited number of cations and anions, the desired physicochemical properties such as thermal stability, miscibility in water or organic solvent, electrochemical potential window, and electric conductivity can be fine-tuned depending on the field of interest. Based on the justification of their chemical behavior, ILs can be divided in two groups namely; aprotic (AILs) and protic (PILs) ILs. AILs are considered to be “classic ILs” and are much more studied than their counterparts, PILs. Interestingly enough, PILs are said to be less expensive than the traditional imidazolium based AIL’s [4].

AILs are mainly based on bulky organic cations such as imidazolium or pyridinium and an assortment of anions such as PF_6^-, Br^-, Cl^-, BF_4^-, $N(CN)_2^-$ [5]. PILs are typically synthesized by proton transfer from a Bronsted acid to a Bronsted base [6]. The most common cations used in PILs include primary, secondary and tertiary ammonium ions whereas the anions are of the organic species such as the carboxylate groups [7]. Common PILs consist of an alkylammonium cation with either an organic or inorganic anion, analogues to the first reported ILs; ethylammonium nitrate and ethanolammonium nitrate [8]. A key characteristic of PILs are their capacity to promote hydrogen bonds, in which includes proton acceptance, proton donation and hydrogen bonding [9,10].

It has been demonstrated that PILs possess lower glass-transition temperatures and melting points compared to AILs. In terms of applications, researchers always tend to analyze the ionic conductivities, densities, melting points, viscosities, and thermophysical properties of PILs [11]. This entails well with its wide-spanned applications in gas separations [12], separating agents in extractive distillation, heat transfer fluids [13], biomass processing [4,14] working fluids in a variety of electrochemical devices (batteries), capacitors, solar cells [15] and biocatalysts [16]. PILs also have been widely used as a Bronsted acid or base [17] in many acid-base-catalyzed organic reactions such as Knoevenagel condensation [18], Diels-Alder reaction [19], Aldol condensation [20], Fischer esterification [21] and Pinacol rearrangement [22] because of their nontoxic, non-volatile and recyclable nature in comparison with mineral acids.

PILs are cheaper to prepare than their counterpart, the AILS. This is due to the simple method for high purity preparation of PILs however, even though they have been known for over a century, only recently has their potential been recognized [23]. In comparison to the work on AILs, there have been very few investigations into the structure of PILs and to date has been limited to the structure of the neat PILs, without the effect of additives being explored. The interest in PILs sparked due to the simple synthesis procedure, low cost of preparation and purification, and also their claimed biodegradable nature [9]. However, the use of any sort of IL requires an in depth knowledge of their thermophysical properties to deem it suitable to be extended from the laboratory to industrial level. The scarce current knowledge of the thermophysical properties of PILs is a barrier for their development for industrial applications [24]. However, apart from good technical performance, the current European Union environmental legislation and REACH (Regulation concerning registration, evaluation, authorization and restriction of chemicals) demands data of the safety of chemicals biodegradation and eco toxicity. As PILs are newly emerging, it is vital to assess their level of hazard before they can be safely employed for use [25]. This review then, encompasses the thermophysical properties of acetate PILs, which includes density, viscosity, speed of sound and

---

***Corresponding author:** Cecilia Devi AP Wilfred, Center of Research in Ionic Liquids (CORIL), Universiti Teknologi Petronas, Bandar Seri Iskandar, Perak 32610, Malaysia, Tel: +6053687635; Fax: +6053656176; E-mail: cecili@petronas.com.my

Received March 17, 2016; **Accepted** May 22, 2016; **Published** May 27, 2016

Citation: Losetty V, Sivapragasam M, Wilfred CDAP (2016) Recent Advances and Thermophysical Properties of Acetate-based Protic Ionic Liquids. Chem Sci J 7: 128. doi:10.4172/2150-3494.1000128

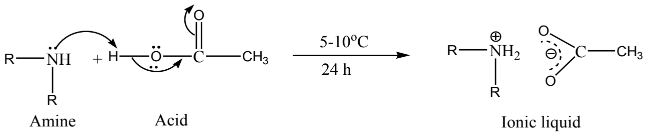
Citation: Losetty V, Sivapragasam M, Wilfred CDAP (2016) Recent Advances and Thermophysical Properties of Acetate-based Protic Ionic Liquids. Chem Sci J 7: 128. doi:10.4172/2150-3494.1000128

decomposition temperatures. Although the properties and applications of PILs have been comprehensively reviewed by Greaves and Drummond their review did not cover the speed of sound properties of PILs as well as its current application [26]. This review then bridges that gap by discussing on various thermophysical properties of acetate PILs as well as current applications.

General Procedure for Synthesis of PILs

PILS and APILs are typically synthesized by various methods like quaternization, neutralization and metathesis methods. Generally, acetate PILs are prepared through the neutralization process, the proton transfer taking place from Bronsted acid to Bronsted base. The reaction mechanism for acetate PILs is given as Scheme 1 and the detailed synthetic procedure for a acetate PILs synthesis is given as follows [27]:

A particular quantity of base was taken in a 100 mL double necked round bottomed flask fitted with a pressure equalizing dropping funnel in an ice bath. An equimolar quantity (stoichiometric quantity) of acetic acid was added drop wise through the dropping funnel at low temperature about 5-10°C in the presence of nitrogen gas. The solution was then stirred to room temperature for 24 h. The main impurity of the IL is water as well as unreacted starting materials. They are removed under high vacuum at about 40°C for 10 h.



Scheme 1: General schematic representation of synthesis of acetate PILs by neutralization method.

Thermophysical Properties of Acetate Based ILs

Density (ρ)

Density is one of the most important properties for any IL or mixture of ILs; which is an important tool to predict the thermophysical properties for process design and solution theories. It is also necessary for many relevant industrial applications such as liquid metering or for the design of equipment like condensers, reboilers, separation trains, or even storage vessels. The density of most ILs is in 1.05-1.35 g.cm^{-3} range at ambient pressure and temperature [28]. The density of the ILs changes with shifts of temperature, also depending on packing of ions, type of anion and cation, size and shape of the ions and ion-ion interactions [26]. The latter statement is satisfactory considering the few ILs with various cations and acetate anion [29-43]. In general, the density decreases gradually with an increase of the alkyl chain length for alkylammonium, alkylimidazolium cations or alkylcarboxylate anions [44] with 1°-amines more likely to have higher densities than 2°- or 3°-amines. The amines which contain other hetero atoms generally exhibit higher density compared to alkylammonium cations. If either cation or anion possesses a hydroxyl group as a substituent, the density increases significantly due to increase of the hydrogen bonding and the decrease of ion-ion separation [45]. For anions containing longer alkyl chains, the density difference is negligible indicating that the increased bulkiness of the hydrocarbon chains keeps the ions separated. From Table 1 it can be observed that density values decreases with an increase in the chain length of the cationic part i.e., N-ethyl-3-methyl imidazolium acetate showed higher density (ρ=1.10190 g.cm^{-3}) data than compare to N-hexyl-3-methyl imidazolium acetate (ρ=1.01700 g.cm^{-3}), the deviation in density is 7.7%. However, 1-butyl ammonium acetate showed lowest density value (0.95644 g.cm^{-3}) while 2-hydroxyethylammonium acetate exhibit highest density value (1.14904 g.cm^{-3}) among all studied ILs. The deviation in density is 16.7% at same temperature and pressure conditions.

Speed of sound (u)

The speed of sound (u) is an important thermodynamic property which can be experimentally determined with precision over a broad range temperature and pressure. The experimental speed of sound relates to other thermodynamic properties such as density, heat capacity, isentropic compressibility, thermal conductivity, isothermal compressibility and excess isentropic compressibility [46]. There are a few theories that explain the nature of these properties and their relationship to each other. These theories reflect as a vital element for the design and optimization of various industrial and engineering processes. The Newton-Laplace's equation states that the relationship between density, speed of sound and isentropic compressibility of liquids [47]; Gardas *et al.* proposed a modified Auerbach's equation which gives well-known empirical relation between the speed of sound, surface tension, and density of ILs [48]; Benson *et al.* explained the connection between density, speed of sound, isentropic compressibility and excess isentropic compressibility of liquids [49] and Rao proposed the relation between speed of sound, temperature and critical temperature of liquids [50].

Normally, the speed of sound decreases with increased temperatures but an increase in the carbon chain on either the cation or anion produces the opposite trend over the speed of sound. While the increment of carbon chain length on the cationic side works in favor of speed of sound, the increment on the anionic side reduces the speed of sound in the ILs [38]. This can be attributed to the increase in spatial distance between molecules due to steric hindrance. Similar trend of decrease in speed of sound with the increase in carbon chain is reported in literature, although there is no universal rule relating the speed of sound to carbon chain length [51]. Table 1 demonstrated that N-methyl-2-hydroxyethylammonium acetate exhibit higher speed of sound (1794.8 ms^{-1}) whereas benzyldimethylammonium acetate showed lower speed of sound (1414 ms^{-1}). The average deviation between these two ILs is 5.5%. Hence, the shape and structure of the IL may influence the resultant speed of sound data.

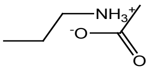
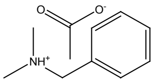
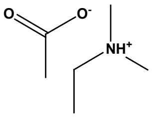
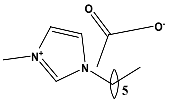
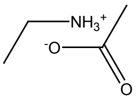
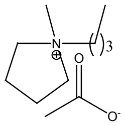
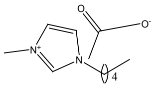
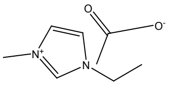
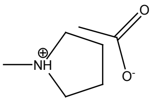
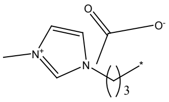
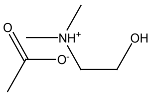
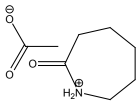
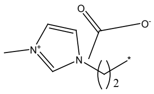
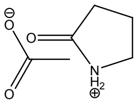
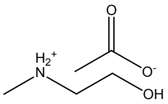
Viscosity (η)

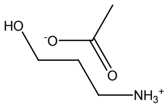
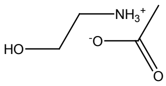
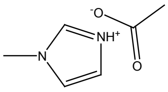
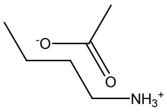
The viscosity normally depends on functional group and chain length of the ILs, with significant reduction in viscosity with the increase in temperature [52]. While viscosity is dependent on ion-ion interactions including Van der Waal's forces and hydrogen bonding [53,54], higher viscosity indicates greater interaction between ions. Table 1, illustrates that an increase in the alkyl chain length of ILs roughly increases the viscosity because of stronger van der Waal's interactions, although delocalization of the charge on anion such as fluorination decreases the viscosity due to weakening the hydrogen bonding [55]. The structure of anion has a large effect on the viscosity, according to Ohno *et al.* [56] an electrostatic interaction force governs the viscosity. Anions which have the larger ionic radius gave the weakest interaction force hence depicting lower viscosity values.

For PILs with alkylammonium cations, it was observed that the viscosity increases with an increase in alkyl chain length and significantly increases with hydroxyl or methyl substitution on to the alkyl chain, (which has been attributed to an increase in the Van der Waal's interaction from the three hydrocarbon chains).

Citation: Losetty V, Sivapragasam M, Wilfred CDAP (2016) Recent Advances and Thermophysical Properties of Acetate-based Protic Ionic Liquids. Chem Sci J 7: 128. doi:10.4172/2150-3494.1000128

Table 1: Full name, chemical structure, densities, speed of sound, viscosity, thermal decomposition temperature and references of acetate PILs.

No	PILs	Chemical structure	ρ/g.cm^{-3}	u/m.s^{-1}	η/mPa.s	T_d/°C	References
1	Propylammonium acetate		0.96682 0.98691	- 1507.96	- 627.41	177 113	[29] [30]
2	Benzyldimethylammonium acetate		0.996864	1414	-	-	[31]
3	*N,N*-dimethyl-*N*-ethylammonium acetate		1.0161	-	14	-	[32]
4	1-hexyl-3-methyl imidazolium acetate		1.01700	-	-	-	[33]
5	Ethylammonium acetate		1.01771	-	-	167	[29]
6	1-butyl-1-methyl pyrrolidinium acetate		1.0212	-	107	-	[32]
7	1-pentyl-3-methyl imidazolium acetate		1.03013	-	-	-	[33]
8	1-ethyl-3-methyl imidazolium acetate		1.0342 1.10190 1.0993 1.09826	- - - 1737	4.95 - 143.6 128.5	- - - 478.4	[32] [33] [34] [35]
9	*N*-methyl-2-pyrrolidonium acetate		1.04606	1473.45	2.622	371	[36]
10	1-butyl-3-methyl imidazolium acetate		1.0523 1.04740 1.05263	- - 1650	297 - 485.1	- - 478.5	[32] [33] [35]
11	*N,N*-dimethyl ethanolammonium acetate		1.0544	1587	-	92	[37]
12	Caprolactam acetate		1.05592	1507.01	29.03	119	[38]
13	1-propyl-3-methyl imidazolium acetate		1.07942	-	-	-	[33]
14	Butyrolactam acetate		1.09535	1496.73	7.84	117	[38]
15	*N*-methyl-2-hydroxyethyl ammonium Acetate		1.10083	1794.8	106.06	-	[39]

16	3-hydroxypropyl ammonium acetate		1.11202	1770.84	2827.01	136	[30]
17	2-hydroxyethylammonium Acetate		1.14339	-	224.68	558.5	[40]*
			1.14904	1790.7	-	-	[41]
18	1-methyl imidazolium acetate		1.07533	-	6.93	-	[42]
19	1-butyl ammonium acetate		0.95644	-	546.35	-	[43]

*303.15 K

The high viscosity data can be observed for a benzene substituted imidazolium PIL due to stacking of benzene rings leading to more ion-ion interactions. Di-substituted imidazolium rings had much higher viscosities than mono substituted rings, which is consistent with the increases in the van der Waal's interaction. The substitution of a methyl group onto the imidazolium ring led to a higher viscosity than with an ethyl group, which has been attributed to the increase in the cation size modifying the interaction between the cation and the anion [57]. From Table 1, butyrolactam acetate showed lower viscosity 7.8 mPa.s and 3-hydroxypropylammonium acetate exhibit higher viscosity 2827.01 mPa.s. Hence, the viscosity of the ILs highly affected by the type of functional group attached to the cation or anion and also its hydrocarbon chain length.

Thermal decomposition temperature (Td)

The thermal stability of ILs commonly depends on the strength of the heteroatom-carbon bond or hetero atom-hydrogen bond. In general, acetate PILs show less thermal stability compared to imidazolium type APILs; this may be due to proton back transfer, which proceeds through equilibrium shifting towards neutral components [58].

The thermal decomposition of hydroxyl ammonium ionic liquids increases with increasing alkyl chain either in the cation or anion. It seems that both cation and anion play a significant role in thermal decomposition of hydroxyl ammonium ionic liquids. The purity of ILs definitely affects the thermal decomposition, as hydroxyl ammonium ionic liquids have tendency to absorb moisture. However, PILs which have carboxylate anions, especially formate, may possess lower thermal stability due to involvement in the condensation reaction to form amides [45,59,60].

Biological and Chemical Applications of Acetate Based PILs

Stereotypically, PILs are widely used for fuel cell applications or as critically reviewed by Yasuda *et al.* [61] and Angell *et al.* [62]. This was based on the concept of PILs having an additional feature provided by the Proton Activity (PA). The reactivity of this mobile active proton makes them the best bet for fuel cell applications [63]. Apart from being widely used for fuel cell applications, its biological applications are slowly but surely emerging. PILs have been suggested as "greener" alternatives to conventional solvents in various industrial applications. This is however employed after a thorough assessment of their toxicity, carcinogenicity, mutagenicity, and environmental impact [23]. Due to the characteristics of PILs being hydrophobic and the capability to form hydrogen bonds, they are excellent candidates for protein solvents [28]. PILs have been shown to be useful in preventing protein aggregation by having weaker attraction to the hydrophobic part of the protein than conventional surfactants, and hence, in low concentrations, it can be displaced more easily during the protein refolding [64]. In a study by Choi and Kwon [60], acetate based PILs was employed for the dissolution zein, an industrially important natural polymer. The aforesaid PILs dissolved zein with ease and were confirmed to be a better candidate than organic solvents, imidazolinium-type ILs and deep eutectic solvents which had been suggested as a solvent for zein. These PILs were also economically viable and environmentally benign. PILs are formed in a one-step reaction from a low cost acid (acetic acid) and base (amine) reagents. The low cost of these acid and base reagents, and the simplicity of PIL synthesis indicates that the production of the PILs to be simpler and more cost-effective as compared to APILs [62]. However, due to a lower degree of protonation of amines by acetic acid, protic acetates were found to be thermally unstable. Another advantage of PILs is that they are easily separated and recycled [64]. This was seen when Achinivu *et al.* employed acetate PILs as a solvent for lignin extraction. To demonstrate this, mixtures of the PILs with Kraft lignin were separated via vacuum distillation and then confirmed that the recovered cellulose largely maintained its cellulose crystal structure due to the low solubility of cellulose in the PILs [64].

In lieu with the current demands on producing green PILs many studies have been skewed towards evaluating the potential toxicity of the PILs. In a study by Peric *et al.* [25] the toxicity and biodegradability of four PILs were investigated. From the main results of this study, it was found that, in general, an elongation of the alkyl chain of the PILs increased the negative impact of these chemicals on the microorganisms tested. Reid *et al.* [23] also assessed then the effect of cation structure on the resulting mutagenicity of the PIL. They found that by increasing the length of the alkyl side chains on the cation ([DMEta][OAc] to [EMEtA][OAc] to [DEEtA][OAc] the mutagenicity index increased consistently.

Other recent applications of PILs include that of lubricant additives. Taaber *et al.* [65] studied a new composite consisting of PIL and copper oxide as a lubricant additive for the first time. Both nanoparticles and PILs were fully soluble and stable in oil and showed remarkable performances with wear reduction up to 47%. PILs were also used to process ionogels or as seen in Trivedi *et al.* [66]. The benefit of the PILs having higher fluidity and conductivity, led to the higher dissolution of agarose and increased the conductivity and mechanical properties of the ionogels.

Huang *et al.* [67] observed that the solubility of H_2S and CO_2 in two PILs (methyldiethanolammonium acetate and dimethylethanolammonium acetate) at 303.2-333.2 K. These ILs showed higher absorption capacity and much lower Henry's law constants for H_2S than for normal ILs (3.5-11.5 bar at 303.2 K). Khonkaen *et al.* [68] have studied an energy requirement and capital investment cost between conventional Mono Ethanol Amine (MEA) and IL-based process. Where, 1-Ethyl-3-methylimidazolium acetate used for the post-combustion carbon dioxide capture, based on the flue gas from coal burning power plant. The results show lower energy requirement of IL-based process compared to MEA-based process by 13.5%, but the investment cost of IL-based process doubles compared to MEA-based process. Stevanovic *et al.* [69] have explained that the mixture of [C_1C_4Pyrro][Ac] with water showed highest CO_2 absorption than compared to pure [C_1C_4Pyrro][Ac] because of the chemical reaction tendency is very less between IL and CO_2. Carvalho *et al.* [70] reported that the binary system of 1-butyl-3-methylimidazolium acetate + CO_2 presents a high CO_2 solubility at low pressures, but as the CO_2 molar fraction increases the solubility decreases exponentially. Gomez-Coma *et al.* [71] reported that absorption of CO_2 using PVDF fibers with 1-ethyl-3-methylimidazolium acetate exhibited higher values than the PVDF hollow fiber membrane contactors using conventional solvents such as MEA and DEA. Li *et al.* [72] investigated the absorption performance of CO_2 in 1-ethyl-3-methylimidazolium acetate [C_2mim][Ac] under the exposure to SO_2 with low concentration through the experimental method and theoretical calculation. Sun *et al.* [73] have studied low ionicity at high temperatures for a series of acetate-based PILs such as diethylammonium acetate, bis(methoxyethyl)ammonium acetate and pyrrolodium acetate, which form neutral components as a result of back proton transfer through an equilibrium shift.

The palladium-catalyzed coupling of olefins with aryl or vinyl halides is called as Heck reaction. Guanidine acetate based ILs are efficient reaction media for palladium-catalyzed Heck reactions. They offers the advantage of high activity and reusability (which played multiple roles in the reaction), as solvents, as strong bases to facilitate β-hydride elimination, and as a ligand to stabilize activated Pd species [74]. Triethylammonium acetate have been employed for the synthesis of 3,4-dihydropyrimidinones in high yield by one-pot three component Biginelli condensation, which acted as catalyst / reaction medium [75]. Zhou *et al.* [76] have investigated the use of chlorine-free metallic acetate ILs as catalysts for the degradation of Poly (ethylene terephthalate) (PET) because of their lower toxicity and cost. Various 2,6-dibenzylidenecycloalkanones were readily prepared in a condensation reaction catalyzed by 2-hydroxyethylammonium acetate ionic liquid under solvent- free conditions. The major advantages of this method are high yields, short reaction times, lack of solvent, and low cost [77]. Methoxypropylammonium acetate ionic liquid has been used as an environmentally benign catalyst for Henry reactions and Knoevenagel reaction of active nitromethane compounds with various aldehydes. These reactions carried out under solvent-free condition, highly effective and very selective, the resultant yield is about 99% [78]. Chin *et al.* [79] have reported DBU based acetate as a catalyst for the synthesis of α,β-unsaturated ketones to N-substituted amines through the Michael reaction. Ying *et al.* [80] have synthesized DBU acetate, used as a catalyst for the synthesis of aromatic amines to α,β-unsaturated ketones through the Aza-Michael reaction.

Conclusion

In this work most relevant thermophysical properties of acetate PILs such as density, speed of sound, viscosity and decomposition temperature were analyzed. Thermophysical data available in current literature are limited to a reduced number of ILs, with most of the data centered on ammonium based cation and acetate anion for all ILs at 298.15 K temperature and atmospheric pressure. The results were often analyzed in terms of nature of the cation, type of substituents attached to cation and alkyl chain length of cation. However, the "greenness" of solvents is always a matter of judgement, as such new challenges lie in creating green PILs. Based on the recent application given in this review for the applications of PILs, it can be safely said the future of "green" PILs is in reach.

Acknowledgements

Authors would like to acknowledge the Center of Research in Ionic Liquids (CORIL), Universiti Teknologi Petronas, Perak, Malaysia for the financial support from Grant No. PRF/0153AB-A30.

References

1. Losetty V, Chennuri BK, Gardas RL (2015) Thermophysical and spectroscopic study of pure N-methylcyclohexylammonium based ionic liquids. J Chem Thermodyn 90: 251-258.
2. Pereiro AB, Rodriguez A (2007) Thermodynamic Properties of Ionic Liquids in Organic Solvents from (293.15 to 303.15) K. J Chem Eng Data 52: 600-608.
3. Wang H, Wang J, Zhang S (2012) Apparent Molar Volumes and Expansivities of Ionic Liquids [$C_n$mim]Br (n = 4, 8, 10, 12) in Dimethyl Sulfoxide. J Chem Eng Data 57: 1939-1944.
4. Rashid T, Kait CF, Regupathi I, Murugesan T (2016) Dissolution of kraft lignin using Protic Ionic Liquids and characterization. Ind Crops Prod 84: 284-293.
5. Peric B, Sierra J, Martí E, Cruañas R, Garau MA, et al. (2013) (Eco)toxicity and biodegradability of selected protic and aprotic ionic liquids. J Hazard Mater 261: 99-105.
6. Anouti M, Caillon-Caravanier M, Dridi Y, Galiano H, Lemordant D (2008) Synthesis and characterization of new pyrrolidinium based protic ionic liquids. Good and superionic liquids. J Phys Chem B 112: 13335-13343.
7. Espinosa T, Sanes J, Jimenez AE, Bermudezn MD (2013) Protic ammonium carboxylate ionic liquid lubricants of OFHC copper. Wear 303: 495-509.
8. Greaves TL, Kennedy DF, Weerawardena A, Nicholas MKT, Kirby N, et al. (2011) Nanostructured Protic Ionic Liquids Retain Nanoscale Features in Aqueous Solution While Precursor Brønsted Acids and Bases Exhibit Different Behavior. J Phys Chem B 115: 2055-2066.
9. Oliveira MV, Vidal BT, Melo CM, de Miranda Rde C, Soares CM, et al. (2016) (Eco)toxicity and biodegradability of protic ionic liquids. Chemosphere 147: 460-466.
10. Ortega Vega MR, Kunst SR, da Silva JAT, Mattedi S, de Fraga Malfatti C (2015) Influence of anion chain length of protic ionic liquids on the corrosion resistance of API X70 steel. Corrosion Eng Sci Tech 50: 547-558.
11. Guo F, Zhang S, Wang J, Teng B, Zhang T, et al. (2015) Synthesis and Applications of Ionic Liquids in Clean Energy and Environment: A Review. Curr Org Chem 19: 455-468.
12. Vila J, Gines P, Pico JM, Franjo C, Jimenez E, et al. (2006) Temperature dependence of the electrical conductivity in EMIM-based ionic liquids Evidence of Vogel Tamman Fulcher behavior. Fluid Phase Equilib 242: 141-146.
13. Ye C, Liu W, Chen Y, Yu L (2001) Room-temperature ionic liquids: a novel versatile lubricant. Chem Commun (Camb) : 2244-2245.
14. Idris A, Vijayaraghavan R, Patti AF, MacFarlane DR (2014) Distillable Protic Ionic Liquids for Keratin Dissolution and Recovery. ACS Sustainable Chem Eng 2: 1888-1894.
15. Ziyada AK, Wilfred CD, Bustam MA, Man Z, Murugesan T (2010) Thermophysical properties of 1-propyronitrile-3-alkylimidazolium bromide ionic liquids at temperatures from (293.15 to 353.15) K. J Chem Eng Data 55: 3886-3890.

16. Zhong Y, Wang H, Diao K (2007) Densities and excess volumes of binary mixtures of the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate with aromatic compound at T = (298.15 to 313.15) K. J Chem Thermodyn 39: 291-296.

17. Ye H, Huang J, Xu JJ, Kodiweera NKAC, Jayakody JRP, et al. (2008) New Membranes Based on Ionic Liquids for PEM Fuel Cells at Elevated Temperatures. J Power Sources 178: 651-660.

18. Nakamoto H, Watanabe M (2007) Bronsted acid-base ionic liquids for fuel cell electrolytes. Chem Commun (Camb), pp: 2539-2541.

19. Darvatkar NB, Deorukhkar AR, Bhilare SV, Salunkhe MM (2006) Ionic Liquid-Mediated Knoevenagel Condensation of Meldrum’s Acid and Aldehydes. Synth Commun 36: 3043-3051.

20. Janus E, Goc-Maciejewska I, Lozynski M, Pernak J (2006) Diels-Alder Reaction in Protic Ionic Liquids. Tetrahedron Lett 47: 4079-4083.

21. Zhu A, Jiang T, Wang D, Han B, Liu L, et al. (2005) Direct aldol reactions catalyzed by 1,1,3,3-tetramethylguanidine lactate without solvent. Green Chem 7: 514-517.

22. Zhou H, Yang J, Ye L, Lin H, Yuan Y (2010) Effects of Acidity and Immiscibility of Lactam-Based Brønsted-Acidic Ionic Liquids on Their Catalytic Performance for Esterification. Green Chem 12: 661-665.

23. Reid JESJ, Sullivan N, Swift L, Hembury GA, Shimizu S, et al. (2015) Assessing the mutagenicity of protic ionic liquids using the mini Ames test. Sustain Chem Process 3: 1-11.

24. Pinto RR, Mattedi S, Aznar M (2015) Synthesis and Physical Properties of Three Protic Ionic Liquids with the Ethylammonium Cation. Chem Eng Trans 43: 1165-1170.

25. Peric B, Martí E, Sierra J, Cruañas R, Iglesias M, et al. (2011) Terrestrial ecotoxicity of short aliphatic protic ionic liquids. Environ Toxicol Chem 30: 2802-2809.

26. Greaves TL, Drummond CJ (2008) Protic ionic liquids: properties and applications. Chem Rev 108: 206-237.

27. Losetty V, Chennuri BK, Gardas RL (2016) Synthesis, spectroscopic characterization and acoustic, volumetric, transport and thermal properties of hydroxyl ammonium based ionic Liquids. J Chem Thermodyn 92: 175-181.

28. Aparicio S, Atilhan M, Karadas F (2010) Thermophysical Properties of Pure Ionic Liquids: Review of Present Situation. Ind Eng Chem Res 49: 9580-9595.

29. Hou M, Xu Y, Han Y, Chen B, Zhang W, et al. (2013) Thermodynamic properties of aqueous solutions of two ammonium-based protic ionic liquids at 298.15 K. J Mol Liq 178: 149-155.

30. Chhotaray PK, Gardas RL (2014) Thermophysical properties of ammonium and hydroxylammonium protic ionic liquids. J Chem Thermodyn 72: 117-124.

31. Gupta AK, Gardas RL (2015) The constitutive behavior of ammonium ionic liquids: a physiochemical approach. RSC Adv 5: 46881-46889.

32. Almeida HFD, Passos H, Lopes-da-Silva JA, Fernandes AM, Freire MG, et al. (2012) Thermophysical Properties of Five Acetate-Based Ionic Liquids. J Chem Eng Data 57: 3005-3013.

33. Ma XX, Wei J, Zhang QB, Tian F, Feng YY, et al. (2013) Prediction of Thermophysical Properties of Acetate-Based Ionic Liquids Using Semi-empirical Methods. Ind Eng Chem Res 52: 9490-9496.

34. Freire MG, Teles ARR, Rocha MAA, Bernd S, Neves CMSS, et al. (2011) Thermophysical Characterization of Ionic Liquids Able To Dissolve Biomass. J Chem Eng Data 56: 4813-4822.

35. Araujo JMM, Pereiro AB, Alves F, Marrucho IM, Rebelo LPN (2013) Nucleic acid bases in 1-alkyl-3-methylimidazolium acetate ionic liquids: A thermophysical and ionic conductivity analysis. J Chem Thermodyn 57: 1-8.

36. Panda S, Gardas RL (2015) Measurement and correlation for the thermophysical properties of novel pyrrolidonium ionic liquids: Effect of temperature and alkylchain length on anion. Fluid Phase Equilib 386: 65-74.

37. Sharma G, Gardas RL, Coronas A, Venkatarathnam G (2016) Effect of anion chain length on physicochemical properties of N,N-dimethylethanolammonium based protic ionic liquids. Fluid Phase Equilib 415: 1-7.

38. Chhotaray PK, Jella S, Gardas RL (2014) Physicochemical properties of low viscous lactam based ionic liquids. J Chem Thermodyn 74: 255-262.

39. Alvarez VH, Dosil N, Gonzalez-Cabaleiro R, Mattedi S, Martin-Pastor M, et al. (2010) Brønsted Ionic Liquids for Sustainable Processes: Synthesis and Physical Properties. J Chem Eng Data 55: 625-632.

40. Kurnia KA, Wilfred CD, Murugesan T (2009) Thermophysical properties of hydroxyl ammonium ionic liquids. J Chem Thermodyn 41: 517-521.

41. Alvarez VH, Mattedi S, Martin-Pastor M, Aznar M, Iglesias M (2011) Thermophysical properties of binary mixtures of {ionic liquid 2-hydroxy ethylammonium acetate + (water, methanol, or ethanol)}. J Chem Thermodyn 43: 997-1010.

42. Qian W, Xu Y, Zhu H, Yu C (2012) Properties of pure 1-methylimidazolium acetate ionic liquid and its binary mixtures with alcohols. J Chem Thermodyn 49: 87-94.

43. 43. Xu Y, Yao J, Wang C, Li H (2012) Density, Viscosity, and Refractive Index Properties for the Binary Mixtures of n-Butylammonium Acetate Ionic Liquid + Alkanols at Several Temperatures. J Chem Eng Data 57: 298-308.

44. Zhou ZB, Matsumoto H, Tatsumi K (2004) Low-melting, Low-viscous, Hydrophobic Ionic Liquids: N-Alkyl (alkyl ether)-N-methylpyrrolidinium Perfluoroethyltrifluoroborate. Chem Lett 33: 1636-1637.

45. Greaves TL, Weerawardena A, Fong C, Krodkiewska I, Drummond CJ (2006) Protic ionic liquids: solvents with tunable phase behavior and physicochemical properties. J Phys Chem B 110: 22479-22487.

46. Queimada AJ, Coutinho JAP, Marrucho IM, Daridon JL (2006) Corresponding-states modeling of the speed of sound of long-chain hydrocarbons. Int J Thermophys 27: 1095-1109.

47. Bonhôte P, Dias AP, Papageorgiou N, Kalyanasundaram K, Grätzel M (1996) Hydrophobic, Highly Conductive Ambient-Temperature Molten Salts. Inorg Chem 35: 1168-1178.

48. Gardas RL, Coutinho JAP (2008) Estimation of speed of sound of ionic liquids using surface tensions and densities: a volume based approach. Fluid Phase Equilib 267: 188-192.

49. Benson GC, Kiyohara O (1979) Evaluation of excess isentropic compressibilities and isochoric heat capacities. J Chem Thermodyn 11: 1061-1067.

50. Rao MR (1941) Velocity of sound in liquids and chemical constitution. J Chem Phys 9: 682-685.

51. Wu KJ, Chen QL, He CH (2014) Speed of sound of ionic liquids: Database, estimation, and its application for thermal conductivity prediction. AIChE 60: 1120-1131.

52. Ziyada AK, Bustam MA, Wilfred CD, Murugesan T (2011) Densities, Viscosities, and Refractive Indices of 1-Hexyl-3-propanenitrile Imidazolium Ionic Liquids Incorporated with Sulfonate-Based Anions. J Chem Eng Data 56: 2343-2348.

53. Muhammad N, Man Z, Ziyada AK, Bustam MA, Wilfred CD, et al. (2012) Thermophysical Properties of Dual Functionalized Imidazolium-Based Ionic Liquids. J Chem Eng Data 57: 737-743.

54. Muhammad A, Abdul Mutalib MI, Wilfred CD, Murugesan T, Shafeeq A (2008) Thermophysical properties of 1-hexyl-3-methyl imidazolium based ionicliquids with tetrafluoroborate, hexafluorophosphate and bis(trifluoromethylsulfonyl) imide anions. J Chem Thermodyn 40: 1433-1438.

55. Bagno A, Butts C, Chiappe C, D’Amico F, Lord JC, et al. (2005) The effect of the anion on the physical properties of trihalide-based N,N-dialkylimidazolium ionic liquids. Org Biomol Chem 3: 1624-1630.

56. Ohno H, Yoshizawa M (2002) Ion conductive characteristics of ionic liquids prepared by neutralization of alkylimidazoles. Solid State Ionics 154-155: 303-309.

57. Gao H, Han B, Li J, Jiang T, Liu Z, et al. (2004) Preparation of Room-Temperature Ionic Liquids by Neutralization of 1,1,3,3-Tetramethylguanidine with Acids and their Use as Media for Mannich Reaction. Synth Commun 34: 3083-3089.

58. Wilkes JS (2004) Properties of ionic liquid solvents for catalysis. J Mol Catal A: Chem 214: 11-17.

59. Bicak N (2005) A new ionic liquid: 2-hydroxy ethylammonium formate. J Mol Liq 116: 15-18.

60. Choi HM, Kwon I (2010) Dissolution of zein using protic ionic liquids: N-(2-hydroxyethyl) ammonium formate and N-(2-hydroxyethyl) ammonium acetate. Ind Eng Chem Res 50: 2452-2454.

61. Yasuda T, Watanabe M (2013) Protic ionic liquids: Fuel cell applications. MRS Bulletin 38: 560-566.

62. Angell CA, Byrne N, Belieres JP (2007) Parallel developments in aprotic and protic ionic liquids: physical chemistry and applications. Acc Chem Res 40: 1228-1236.

63. Byrne N, Angell CA (2008) Protein unfolding, and the “tuning in” of reversible intermediate states, in protic ionic liquid media. J Mol Biol 378: 707-714.

64. Achinivu EC, Howard RM, Li G, Graczb H, Henderson WA (2014) Lignin extraction from biomass with protic ionic liquids. Green Chem 16: 1114-1119.

65. Taaber T, Enok AE, Joost U, Oras S, Jarvekulg M, et al. (2015) Tribological properties of protic ionic liquid and functionalized copper oxide nanoparticles as additives to base oil. Mechanika 21: 148-153.

66. Trivedi TJ, Srivastava DN, Rogers RD, Kumar A (2012) Agarose processing in protic and mixed protic–aprotic ionic liquids: dissolution, regeneration and high conductivity, high strength ionogels. Green Chem 14: 2831-2839.

67. Huang K, Zhang XM, Xu Y, Wua YT, Hu XB (2014) Protic ionic liquids for the selective absorption of H_2S from CO_2: Thermodynamic analysis. AIChE J 60: 4232-4240.

68. Khonkaen K, Siemanond K, Henni A (2014) Simulation of Carbon Dioxide Capture Using Ionic Liquid 1-Ethyl-3-methylimidazolium Acetate. ESCAPE 24: 1045-1050.

69. Stevanovic S, Podgorsek A, Moura L, Santini CC, Padua AAH, et al. (2013) Absorption of carbon dioxide by ionic liquids with carboxylate anions. International Journal of Greenhouse Gas Control 17: 78-88.

70. Carvalho PJ, Alvarez VH, Schröder B, Gil AM, Marrucho IM, et al. (2009) Specific solvation interactions of CO_2 on acetate and trifluoroacetate imidazolium based ionic liquids at high pressures. J Phys Chem B 113: 6803-6812.

71. Gomez-Coma L, Garea A, Rouch JC, Savart T, Lahitte JF, et al. (2016) Membrane modules for CO_2 capture based on PVDF hollow fibers with ionic liquids immobilized. J Membr Sci 498: 218-226.

72. Li X, Zhang L, Zheng Y, Zheng C (2015) Effect of SO_2 on CO_2 Absorption in Flue Gas by Ionic Liquid 1-Ethyl-3-methylimidazolium Acetate. Ind Eng Chem Res 54: 8569-8578.

73. Sun X, Liu S, Khan A, Zhao C, Yana C, et al. (2014) Ionicity of acetate-based protic ionic liquids: evidence for both liquid and gaseous phases. New J Chem 38: 3449-3456.

74. Li S, Lin Y, Xie H, Zhang S, Xu J (2006) Brønsted guanidine acid-base ionic liquids: novel reaction media for the palladium-catalyzed Heck reaction. Org Lett 8: 391-394.

75. Attri P, Bhatia R, Gaur J, Arora B, Gupta A, et al. (2014) Triethylammonium acetate ionic liquid assisted one-pot synthesis of dihydropyrimidinones and evaluation of their antioxidant and antibacterial activities. Arabian J Chem.

76. Zhou X, Lu X, Wang Q, Zhu M, Li Z (2012) Effective catalysis of poly(ethylene terephthalate) (PET) degradation by metallic acetate ionic liquids. Pure Appl Chem 84: 789-801.

77. Kang LQ, Cai YQ, Wang H, Li LH (2014) Solvent-free catalytic preparation of 2,6-dibenzylidenecycloalkanones using 2-hydroxyethylammonium acetate ionic liquid as catalyst. Monatsh Chem 145: 337-340.

78. Wang WJ, Cheng WP, Shao LL, Liu CH, Yang JG (2009) Henry and Knoevenagel Reactions Catalyzed by Methoxyl Propylamine Acetate Ionic Liquid. Kinet Catal 50: 186-191.

79. Chen X, Ying A (2013) DBU Derived Ionic Liquids and Their Application in Organic Synthetic Reactions. Chem Inform 44: 305-330.

80. Ying AG, Wang LM, Deng HX, Chen JH, Chen XZ, et al. (2009) Green and efficient aza-Michael additions of aromatic amines to α,β-unsaturated ketones catalyzed by DBU based task-specific ionic liquids without solvent. ARKIVOC 11: 288-298.