

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

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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^- , $\text{N}(\text{CN})_2^-$ [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 ethanolanmonium 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

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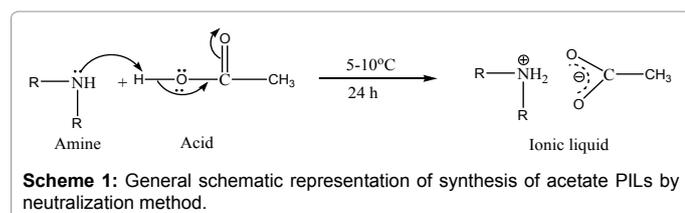
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decomposition temperatures. Although the properties and applications of PILs have been comprehensively reviewed by Greaves and Drummond their review did not cover the speed of sound properties of PILs as well as its current application [26]. This review 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 an 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.



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 ($\rho=1.10190$ g.cm⁻³) data than compare to N-hexyl-3-methyl imidazolium acetate

($\rho=1.01700$ 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].

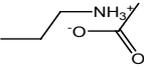
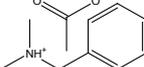
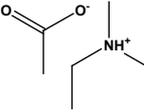
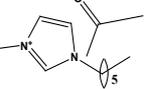
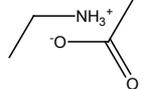
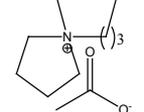
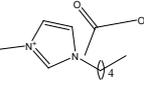
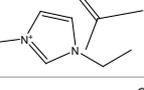
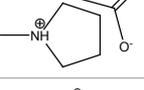
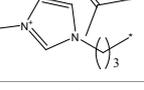
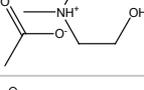
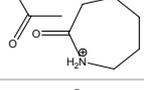
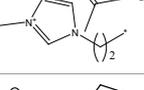
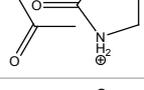
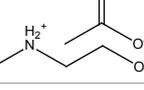
Normally, the speed of sound decreases with increased temperatures but an increase in the carbon chain on either the cation or anion produces the opposite trend over the speed of sound. While the increment of carbon chain length on the cationic side works in favor of speed of sound, the increment on 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 benzyltrimethylammonium 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.

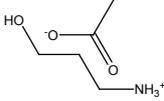
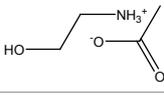
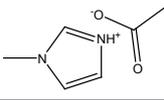
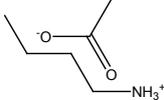
Viscosity (η)

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).

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

No	PILs	Chemical structure	$\rho/\text{g.cm}^{-3}$	$u/\text{m.s}^{-1}$	$\eta/\text{mPa.s}$	$T_d/^\circ\text{C}$	References
1	Propylammonium acetate		0.96682 0.98691	- 1507.96	- 627.41	177 113	[29] [30]
2	Benzyltrimethylammonium acetate		0.996864	1414	-	-	[31]
3	<i>N,N</i> -dimethyl- <i>N</i> -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	<i>N</i> -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	<i>N,N</i> -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	<i>N</i> -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, imidazolium-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 H₂S and CO₂ 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 H₂S 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 [C₁C₄Pyrro][Ac] with water showed highest CO₂ absorption than compared to pure [C₁C₄Pyrro][Ac] because of the chemical reaction tendency is very less between IL and CO₂. Carvalho *et al.* [70] reported that the binary system of 1-butyl-3-methylimidazolium acetate + CO₂ presents a high CO₂ solubility at low pressures, but as the CO₂ molar fraction increases the solubility decreases exponentially. Gomez-Coma *et al.* [71] reported that absorption of CO₂ 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 CO₂ in 1-ethyl-3-methylimidazolium acetate [C₂mim][Ac] under the exposure to SO₂ 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 pyrrolodinium 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-dibenzylidene-cycloalkanones 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.

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