

# pH and electrical conductivity measurements of aqueous solutions of amino acid-based ionic

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**Abstract.** Ionic liquids are promising materials for several applications. Amino acid based ionic liquids (AAILs) as a sort of a new generation of ionic liquids are recently proposed taking advantage of hydrogen bonding group and low toxicity. Three types of AAILs are examined in this work; namely 1-Octyl-3-Methylimidazolium Glycine [OMIM][Gly], 1-Octyl-3-Methylimidazolium Alanine [OMIM][Ala] and 1-Octyl-3-Methylimidazolium Proline [OMIM][Pro]. The pH and molar conductivity are measured at ambient conditions for AAILs aqueous solutions at different concentrations; specifically 1, 10, 20, and 30 wt.%. The experimental results show that all AAILs solutions are alkaline (pH>7) where [OMIM][Pro] has the highest pH compared to its counterparts. The trend is reversed for molar conductivity as [OMIM][Gly] showed the highest molar conductivity. These results are attributed to the smaller size of [Gly] compared to [Pro] and [Ala]. However, adding AAILs increases the molar conductivity of the water.

## 1 Introduction

Over the past decade, ionic liquids (ILs) have attracted immense attention as green solvent due to their low vapor pressure, high thermal-chemical stability, non-flammability, and cation and anion are tunable, that gives less impact on the health, safety, and environment [1–3]. ILs have been investigated for several applications such as catalyst, solvent, CO<sub>2</sub> capture, and gas hydrates inhibition [4–10]. Recently, the researchers are focusing on producing a new generation of ILs that can overcome the disadvantages of conventional ILs such as toxicity [11–13]. Amino acid based ionic liquids (AAILs) are derived from naturally occurring amino acids and consist of amino acid as anions or cations combined with other conventional cation and anions. In fact, AAILs are liquid at room temperature possess the characteristics of enhancing biological activity and biodegradability [14, 15]. The AAILs properties have tested for useful application in several fields of bulk chemical processing of CO<sub>2</sub> capture, chiral catalysis, and peptide synthesis [16, 17].

The first preparation of AAILs was in 2005 by Fukumoto et. al, where the 1-ethyl-3-methylimidazolium cation ([C<sub>2</sub>mim]) was combined with 20 different types of amino acids [18]. They reported that these AAILs were prepared with amino acids as cations and nitrate as anions [15]. Despite AAILs have dual-functional groups [19], their application constrained by several properties such as their high viscosity and low thermal stability [14, 18, 20].

The physical and chemical properties of ILs should be well-studied prior to any industrial application. As

mentioned earlier, the advantage of AAILs was based on both the side-chain structure of amino acid [30], which highly related to thermophysical properties. Furthermore, ILs properties depend greatly on the cation and anion charging components to ensure that specific symmetry conditions are present. For example, the density measurement found in the descending order of [OMIM][Ser] > [OMIM][Gly] > [OMIM][Ala] where their values were also comparatively lower than published data for AAILs with short alkyl chain length [21]. Papanca et. al, described that the electrical conductivity of the ILs of aqueous solution increased with the decrease in the length of the hydrocarbon chain that attached to the imidazolium ring [22].

In this work, the pH, electrical conductivity, and molar conductivity were reported for three AAILs namely, ; 1-Octyl-3-Methylimidazolium Glycine [OMIM][Gly], 1-Octyl-3-Methylimidazolium Alanine [OMIM][Ala] and 1-Octyl-3-Methylimidazolium Proline [OMIM][Pro]. The ionic liquid solutions were prepared at different concentrations in the range of 1-30 wt.%. The measurements were conducted at ambient conditions where atmospheric pressure and room temperature.

## 2 METHODOLOGY

### 2.1 Materials and Solution Preparation

Three amino acids-based ionic liquids have been synthesized in Centre of Research in Ionic Liquids (CORIL) by combining 1-Octyl-3-Methylimidazolium as

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a cation with different amino acids as an anion. The synthesis method was reported in previous work [23]. The only chosen cation is 1-Octyl-3-Methylimidazolium [OMIM]<sup>+</sup> while the chosen anions are Glycine [Gly]<sup>-</sup>, Alanine [Ala]<sup>-</sup> and Proline [Pro]<sup>-</sup>. The type of ionic liquids, the abbreviations of each AAIL, molecular weight, and purity are presented in Table 1.

**Table 1:** AAILs used in this work with molecular weight (M.W) and purity.

ILs	Abbreviation	M.W (g.mol <sup>-1</sup> )	Purity (%)
1-Octyl-3-Methylimidazolium Glycine	[OMIM][Gly]	269.4	≥99
, 1-Octyl-3-Methylimidazolium Alanine	[OMIM][Ala]	283.4	≥99
1-Octyl-3-Methylimidazolium Proline	[OMIM][Pro]	309.4	≥99

The aqueous solutions are prepared using deionized water at four different concentrations of 1wt%, 10wt%, 20wt%, and 30wt%. Analytic balance with ±0.001 g accuracy is used to weight the sample solutions and kept in airtight containers.

## 2.2 Equipments and procedure

### 2.2.1 pH Measurement

The pH of each AAIL is measured using SevenCompact™ S220 pH meter which supplied by Mettler Toledo. The probe of this meter measures the pH value by the accuracy of pH ±0.002 and temperature ±0.1 °C. The experiments were conducted at conditions of room temperature (25 °C) and atmospheric pressure. The electrode graphite cell was immersed directly into ionic liquid solutions and once the reading has been stabilized then the data was recorded accordingly. The equipment was calibrated using a specific buffer according to the manufacturer instructions. Then, experiment was conducted at four different concentrations of 1wt%, 10wt%, 20wt%, and 30wt%. The reported pH values are the average of three measurements.

### 1.1.2 Conductivity Measurement

Conductivity measurement was conducted using SevenCompact™ S230 electrical conductivity meter which supplied by Mettler Toledo. The probe of this meter measures the electrical conductivity value by the accuracy of conductivity ±0.5 % and temperature ±0.1 °C. The equipment was calibrated by using standard solution provided by the manufacturer. The experiments were conducted at room temperature (25 °C) and atmospheric

pressure. The electrode graphite cell was immersed directly into ionic liquid solutions and the reading has been recorded. This experiment was conducted at four different concentrations of 1wt%, 10wt%, 20wt%, and 30wt%. The average values were reported from three data measurements.

The electrical conductivity results were divided by the molarity to get molar conductivity  $\Lambda$  as shown in Eq. 1.

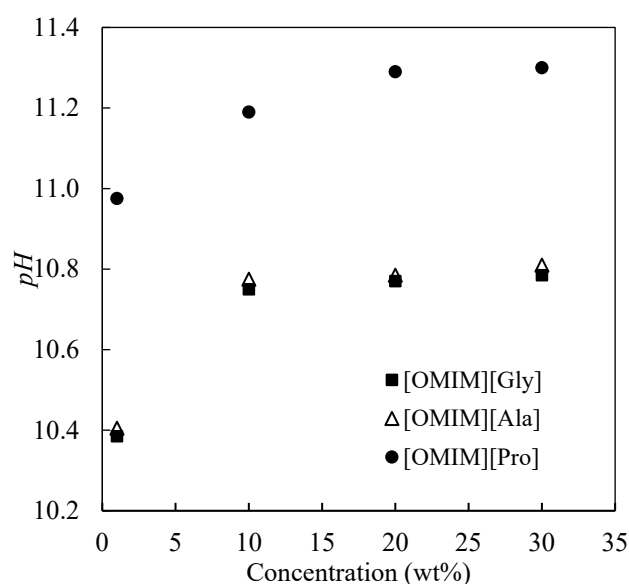
$$\Lambda = \left(\frac{\kappa}{M}\right) \quad (1)$$

where  $\Lambda$  is the molar conductivity (S.cm<sup>2</sup>/ mol), M is the molarity of the AAIL solution (mol/cm<sup>3</sup>), and  $\kappa$  is the measured electrical conductivity (S/cm).

## 3 Results and discussion

### 3.1 pH of AAILs solutions

pH measurements are carried out for four different concentrations of 1wt%, 10wt%, 20wt%, and 30wt% of [OMIM][Gly], [OMIM][Ala], and [OMIM][Pro] aqueous solutions at atmospheric pressure and room temperature (25 °C). Based on the results presented in Fig. 1, all AAIL increase the pH of water (7.74 as measured in this study) and show alkaline behaviour (pH>7) which indicate to the presence of OH<sup>-</sup> in the solution.



**Fig. 1:** pH measurement of AAILs solutions with respect to concentration.

As the [OMIM][AA] dissolved in the water, it will be ionized into their cation [OMIM]<sup>+</sup> and anion [AA]<sup>-</sup>. As the amino acid is negatively charged, it will attract the hydrogen of water molecules and produce more OH<sup>-</sup> in the solution. The cation [OMIM]<sup>+</sup> does not form strong hydrogen bond with OH<sup>-</sup> due to long alkyl chain, which increase its steric hindrance and hydrophobicity.

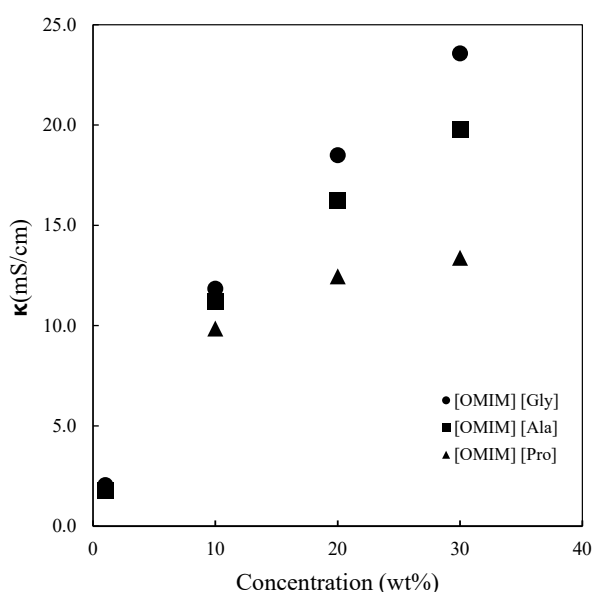
Therefore, it seems that the  $[AA]^-$  is responsible for pH of the solution. This finding was confirmed by comparing the  $pK_b$  values of AA and the studied AAIL. It is well known that the smaller the value of  $pK_b$ , the higher the value of  $K_b$ , the stronger the base is. The values of  $pK_b$  listed in the table are directly proportional to the pH values of AAIL which confirmed that the pH of the solution dominated mainly by AA.

**Table 2:**  $pK_b$  values of amino acid

Amino acid (AA)	$pK_b$
Glycine	9.60
Alanine	9.69
Proline	10.60

### 3.2 Electrical and molar conductivity of AAILs solutions

The electrical conductivity is measured for four different concentrations of 1wt%, 10wt%, 20wt%, and 30wt% of [OMIM][Gly], [OMIM][Ala], and [OMIM][Pro] aqueous solutions at atmospheric pressure and room temperature (25 °C). The data is used to calculate the molar conductivity following eq.1. As the conductivity measure the ability of the solution to conduct electricity, adding AAILs increase charge carries' concentration, Hence, the electrical conductivity increased compared to water. In addition, the electrical conductivity of [OMIM][Gly] aqueous solution represented as highest conductivity if compared to [OMIM][Ala] and [OMIM][Pro] as shown in Table 3 and Fig. 2.



**Fig. 2.** Electrical conductivity measurement of AAILs solutions with respect to concentration.

**Table 3:** Molar conductivity of AAIL solutions

AAILs	1 wt%	10 wt%	20 wt%	30 wt%
[OMIM][Gly]	55.12	31.72	24.60	20.72
[OMIM][Ala]	51.08	31.60	22.75	18.34
[OMIM][Pro]	49.59	30.29	18.98	13.49

In fact, when the dissociation of AAIL in water occurs, several conditions will be influenced such as the ion concentration and charge. As glycine has smaller size due to short side chain and lower molecular weight compared to other AA-, it enhances the electrical conductivity and molar conductivity as the mobility is faster. In addition, shorter alkyl chain could lower agglomeration tendency caused by hydrocarbon chains interaction. It is worth to note that the increase in the concentration results in increasing the conductivity due to the presence of additional electrolytes that contribute in conducting the electricity. Since the increase of molar concentration is not proportional to the increment of conductivity, however, the molar conductivity decreased with increasing the concentration according to equation (1).

## 4 CONCLUSIONS

pH and conductivity measurements of three types of AAILs at four different concentrations were investigated in this work. All AAILs solutions showed alkaline nature. [OMIM][Pro] demonstrated the highest pH value. The amino acid presented as anion in AAILs found to be the controlling factor in pH value. The conductivity measurement also influenced by type of amino acid. [OMIM][Gly] has the highest conductivity due to its smaller size and molecular weight. Increasing the concentration resulted in increase of number of ions, hence, the electrical conductivity increases.

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