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Using a Streamlined Procedure to Combine AlCl3 and Chloroacetamide to Create a New Ionic Liquid

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Abstract

By reacting AlCl3 with chloroacetamide (CA) at the optimal mole ratio (2:1), a new type of ionic liquid was created in addition to the group of ionic liquids (aluminum chloride-amide). With an ionic conductivity of 0.34 mS/cm, the resultant clear brown ionic liquid demonstrated good thermal stability at ambient temperature in a glove box filled with nitrogen gas. Its coordination was established using FT-IR. Measurements have been made of additional physical characteristics including viscosity and cyclic voltammetry.

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1. Introduction

There is rapid race research on ionic liquids based on aluminum compounds with amides is rapidly progressing due to their clear and documented effects in the field of science and advanced technology, which depend on their multiple applications in electrochemistry [1-3], such as batteries, catalysts [4], reactions, and biotechnology processing [5-6]. In general, ionic liquids depend in their preparation on mixing anhydrous AlCl3 with amides forming complexes. These complexes have a coordinated structure that allows the transformation of their solid components into a liquid containing positive and negative ions, such as the AlCl3/Amides ionic liquid studied by Hadi M. A. Abood and Andrew P. Abbott et al [7]. In these cases, aluminum metal behaves as a Lewis acid, forming anionic species such as AlCl4- and Al2Cl7-, which are largely affected by the cationic species of the Lewis base in the liquid. The reaction between AlCl3 and Amides ligands forms anionic and cationic species according to the following equation [7-9]:

$$xAlCl_3 + y\ Amide \leftrightarrow [Alx\text{-}1Cl_3x\text{-}4(Amide)y]^+ + AlCl_4 \quad \ldots(1)$$

2. Materials and Methods

Both chloroacetamide (Sigma-Aldrich) and aluminum chloride anhydrous (Carlo Erba) were utilized without additional purification. Bruker Optik FTIR Spectrometer, was used to obtain infrared spectra. While measuring viscosity manually with a Cannon Viscometer (USA), conductivity was measured with a WTW cond-720 (Germany) instrument in mS/cm. The Instrument for Cyclic voltammogram (CV) was recorded by using a three-electrode system Digi-lvy-Dy2300 Bipotentiostat comprising platinum plat as working electrode (WE), a platinum disc of 2 mm diameter as a counter electrode (CE), and wire of silver as a reference electrode (RE). Dynalon Digital Melting Point Device was used to calculate the melting point (USA).

2.1 Preparation aluminum chloride anhydrous-chloroacetamide ionic liquid:

AlCl3 anhydrous (m.p. 192.4 °C) and chloroacetamide (m.p. 120 °C) were combined to create a novel ionic liquid that contains both substances in varying mole ratios. They were both heated at 50 °C for four hours in a glove box filled with nitrogen gas with constant mechanical stirring until they combined to form a brown homogenous liquid [7]. To reach room temperature, the created ionic liquid is then chilled and kept in an airtight container (Figure 1). This ionic liquid's samples were utilized for further identification.

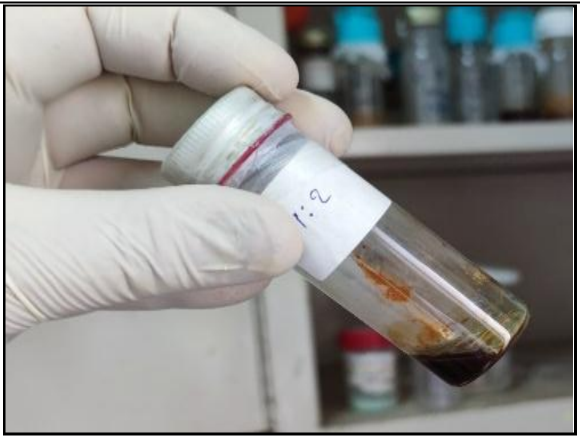

Figure 1. Digital photo of AlCl3:CA (2:1 molar ratio) IL.

3. Results and Discussion

Table 1 below shows, at 27 °C, the mole ratio composition, melting point, and conductivity of chloroacetamide ionic liquid and anhydrous aluminum chloride.

Table 1. Show the mole ratio composition, melting point, and conductivity of ionic liquid at 27 ºC.

No.	The mole ratio of $AlCl_3$:CA	Melting point ºC	Physical state at 27 ºC	Viscosity cP	Conductivity mS/cm
1	1.5:1	52	sold	–	–
2	1.7:1	45	sold	–	–
3	1.8:1	–	liquid	84.265	0.36
4	1.9:1	–	liquid	79.338	0.39
5	2:1	–	liquid	64.183	0.42
6	2.1:1	–	liquid	98.641	0.29
7	2.2:1	48	sold	–	–
8	2.3:1	57	sold	–	–
9	2.5:1	65	sold	–	

The direct relationship between increasing in conductivity with the increasing aluminum chloride molar percentage, can be clearly observed, and this may be attributed to the inclination of Eq. (1) towards the direction of formation of $AlCl_4^-$, $Al_2Cl_7^-$ ions. After that, the inverse relationship begins to appear at the ratio 2.1, where the percentage of aluminum chloride was increased and the electrical conductivity decreased due to the increases in the viscosity of the ionic liquid [9]. Generally, the ionic conductivity [10] can be calculated according to the Arrhenius Eq. (2) and using the graph (Figure 2), where *Ea* is the activation energy, *A* is a coefficient T is temperature, and R is the universal gas constant. A calculated average Ea of the AlCl3:CA ILs is 48.2 kJ/mol.

$$\sigma = Ae - Ea(\sigma)/(RT) \quad \ldots(2)$$

the activation energy was calculated to show whether the energy value was positive or negative to see if there were collisions between the molecules or any interaction that causes a defect in the merging of the two substances (AlCl3 and chloroacetamide) to form the ionic liquid, as well as to prove that there is a flow in the transmission of electrons when using the ionic liquid in electrical applications.

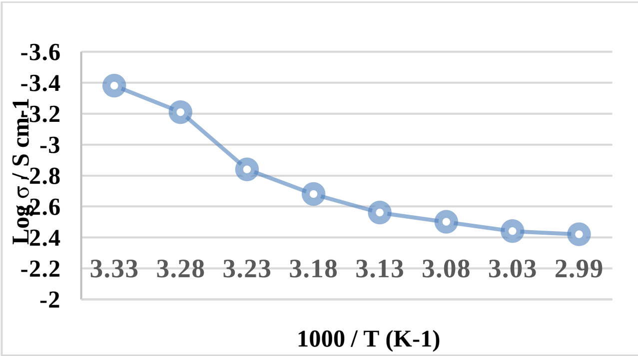

Figure 2. ionic conductivities of $AlCl_3$:CA ionic liquids (2:1 molar ratio) and Temperature (from 27 to 60 °C) to determine the activation energy by the Arrhenius equation.

The important role of the FTIR test is to find out the interaction and coordination [11] between the two solid materials aluminum chloride and chloroacetamide, that formed the ionic liquid. By reading the given frequencies within the Figure 3, where noticed the rise and fall of some vibration frequencies values, which indicates coordination and clear interaction within (2:1) molar ratio. Where, the carbonyl group ν(C=O) vibration frequency transformed from 1616 cm^{-1} to 1668 cm^{-1} with a shift of 52 cm^{-1} to a higher frequency than in alone chloroacetamide and the peak at 760 cm^{-1} can be attributed to C–Cl stretching vibration of chloroacetamide (blue), which converts wider after coordination with aluminum chloride. As for the C-H wagging and twisting vibration peaks shifted from 1096 and 1255 for chloroacetamide to 1102 and 1266 cm^{-1} after coordination with AlCl3, respectively. The extending frequencies of ν(N–H) for CA also suffered a red shift and tensity changing in IL for the symmetrical and asymmetric vibration. Where, the main explanation for these changes in the recent frequency readings may be due to the formation of hydrogen bonds with (NH). Recent research has shown that increasing the acidity of the ionic liquid leads to a change in the frequencies of the main peaks of the components of that liquid. [12].

Figure 4 shows the electrochemical potential window of cyclic voltammogram for $AlCl_3$:CA new IL (2:1 mole ratio) on a platinum working electrode under a scan rate of 0.1 V/s at room temperature. The cyclic voltammetry range of the ionic liquid was between –1.00 V to + 1.3 V and the electrochemical window was 2.3 V. A characteristic "nucleation loop" is also observed for the above new IL [13-14].

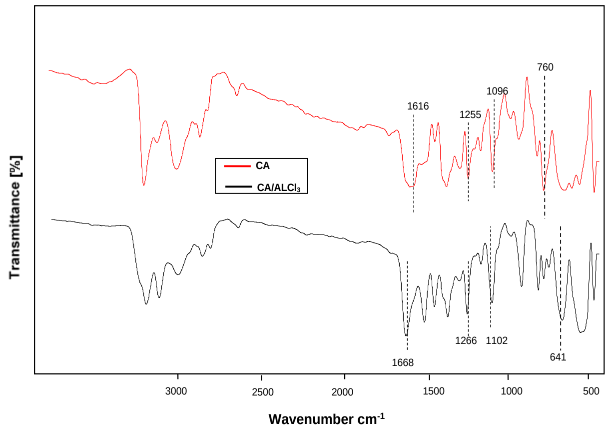

Figure 3. FTIR spectra of Chloroacetamide $ALCl_3$:CA new IL.

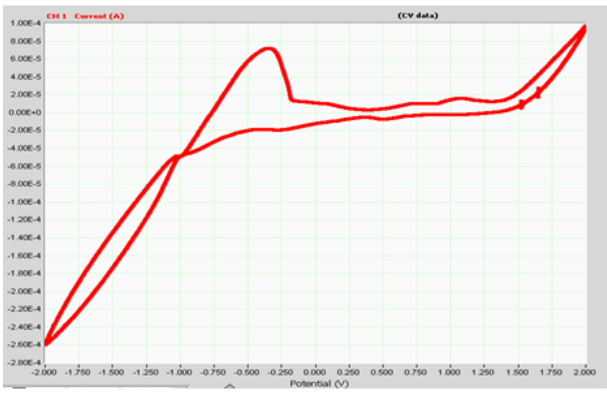

Figure 4. Cyclic voltammogram of $AlCl_3$:CA at 2:1 mole ratio on a platinum working electrode with platinum wire counter and silver reference electrode. Start potential: 1.0 V. Scan rate: 0.1V/s.

4. Conclusions

In this article, a new ionic liquid was prepared from (Aluminum Chloride-Chloroacetamide) which is part of the aluminum chloride-amide family series. Where the ideal molar ratio for mixing was determined by (2:1) respectively, and this ratio was chosen because it gave the lowest viscosity (64.183 cP) and the highest conductivity and stability. And to find out if there is interaction and between the two solid compounds, FTIR tests were done, which showed the coordination between the two compounds by changing the vibration frequencies and changing the values of the obtained peaks. And to prove that the prepared ionic liquid is among other liquids and carry the same properties, viscosity test was conducted against temperature, which proved that the new liquid has characteristics that do not deviate from the nature and properties of other liquids. In addition, the new ionic liquid gave thermal stability and conductivity up to (0.42 mS/ cm) which is considered within the measured conductivity of other ionic liquids. It is possible to candidate this new liquid for another set of physical and chemical tests to be included in the multiple applications of ionic liquids

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