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Synthesis, Characterization and Theoretical Study of the New Aluminate Ionic Liquid: Tetrahepthylammonium-bromotrichloroaluminate $[(C_7H_{15})_4N]^+[AlCl_3Br]^-$

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ABSTRACT

The synthesis of Tetrahepthylammoniumbromotrichloroaluminate ionic liquid (IL) is reported here. The product was characterized by spectroscopic and analytical methods such as FT-IR ^{13}C-NMR, ^{1}H-NMR,^{81}Br-NMR and Mass spectroscopy. The results show that this IL has excellent thermal stability below 110æ%C. Along with the experimental study; this compound has been studied computationally at the B3LYP/LANL2DZ level of theory using the Gaussian 98 program package. From these calculations, optimized geometries, molecular parameters, and vibrational spectra of IL have been calculated. In addition, calculated frequencies are compared with the experimental frequencies after correction by the appropriate scaling factor. This comparison shows that our theoretical data are in good agreement with the experimental results.

Key words: Aluminate; Frequency; Ionic liquid; Room temperature.

INTRODUCTION

At the end of twentieth century, scientists found that unlike traditional view about the melting points of salts, there is a class of salts or salt mixtures those have melting points below 115æ%C, which are referred as ionic liquids[1]. Room-temperature ionic liquids (RTIL)[2] are ionic liquids with melting points at or below room temperature[3]. Some ionic liquids (RTIL) are nonflammable, nonvolatile, or thermally stable and can be used as a promising replacement for the traditional organic solvents. Moreover, many workers have synthesized and studied about ionic liquids. The ionic liquids in organic reaction are often obtained as organic product in these reactions and these can be removed easily from the ionic liquid by extraction with organic solvent without resorting to an aqueous workup or solvent evaporation

It is noteworthy that ionic liquids have been applied for many other purposes. For example, during past years, ionic liquids have been applied to synthesize different compounds[4], polymerization processes, dye synthesis, supercritical fluid chromatography, and determination of phenothiazine derivatives, preparation of sensors and biosensors, preparation of nanostructures, and other applications[5].

However, recent reports indicated that several ionic liquids have been applied to separate various mixtures[6-7]. Moreover, ionic liquid properties such as heat capacities and refractive index[8], luminescence properties[9], osmotic coefficients[10], enthalpy, density, heat capacity[11], and thermophysical properties[11] have been studied since their first synthesis. Therewith, following our previous studies on ionic liquids' chemistry[13-15], we decided to improve our knowledge about these compounds by synthesis, characterization, and theoretical the study of a new aluminum-based ionic liquid. This is useful when a metal catalyst is used in the reaction that is this catalyst often remains in the ionic liquid and can be directly reused. In addition, ionic liquids as a class of novel environmental "green solvents," have remarkable new properties and promising applications in many fields. The first RTIL, ethyl ammonium nitrate (mp 13-14°C), was reported in 1914. However, ionic liquids did not draw much attention till 1992, when Wilkes and coworkers reported air- and water-stable RTILs based on imidazolium salts. Subsequently, research on their synthesis, properties, and applications has increased substantially.

In this work, the synthesis, structural, bonding, thermal solubility, and vibrational properties, and computational the study of a new aluminate IL has been reported. From the results, calculated molecular parameters and vibrational frequencies are shown.

There is continued interest in the development of the new ionic liquid. We think that this paper and the compound reported in it could be found various applications in the oriental.

EXPERIMENTALS

Materials and Instruments

Starting materials were obtained from Merck and were used without further purification.

Solvents were purified by standard methods. Organic solvents were reagent grade. The IR spectrum was recorded using FTIR Bruker Tensor 27 spectrometer. All the chemical shifts are quoted in ppm using the high-frequency positive convention. The percent composition of elements was obtained from the Microanalytical Laboratories, Department of Chemistry, OIRC, Tehran.

Synthesis of Tetrahepthylammoniumbromotrichloroaluminate $[(C_7H_{15})_4N]^+[AlCl_3Br]^-$ Tetrahephylammoniumbromotrichloroaluminate $[(C_7H_{15})_4N]^+[AlCl_3Br]^-$, prepared by this method:

In a 100-mL round-bottom flask, dry Tetrahepthylammoniumbromide(0.39g, 0.80mmol) was dissolved in dry acetonitrile (20 mL) and was stirred for 30 min, while the mixture wasstirring for 5 minutes. $AlCl_3$ (0.11g, 0.82mmol) in acetonitrile added to this mixture as the last of starting materials and stirring was continued for 4 h to precipitate a white solid. A white Precipitate changed to yellow one and was filtered and washed with ether and hexane.m.p.: 100-101°; Anal. Calc. for $[(C_7H_{15})_4N]^+[AlCl_3Br]^-$: Calculated C, 53.88; H, 9.62;N, 2.24Found: C, 53.96; H, 9.88; N, 2.45 IR (KBr) (cm^{-1}): For cation$[(C_7H_{15})_4N]^+$: 3409, 3315, 3225, 3010, 2924, 2874, 2858, 2358, 2765, 2350, 1950, 1458, 1378, 1160, 1091, 463, 453 cm^{-1}, For anion $[AlCl_3Br]^-$: 1052, 764, 900cm^{-1}. ^{13}C-NMR (135 MHz, $CDCl_3$): C_h= 21.87 ppm, C_c= 21.67 ppm, $C_{e,d}$= 26.27 ppm, C_f = 28.75 ppm. ^{1}H-NMR (135 MHz, $CDCl_3$)M= 3.15 ppm, M= 1.69ppm^{81}Br-NMR (135 MHz, $CDCl_3$): ä= 83.217 ppm (Figure 1, 2, 3, 4)

Computational Method

We applied the DFT method to optimize and calculate molecular properties of synthesized compounds. All calculations were done by using the Gaussian 98 programs. For DFT, Becke's three-parameter exchange functional was used in combination with the Lee–Yang–Parr correlation functional (B3LYP) with LANL2DZ basis set. Ionic molecule was used without any symmetry restriction. Calculations were done in the gas phase. After the optimization procedures, frequency calculations were done to extract vibrational mode and test the correctness of true minima. The vibrational frequencies and intensities (spectra) and the eigenvectors for the normal modes were corrected with the appropriate factor and displayed on a computer screen to identify the dominating motions.

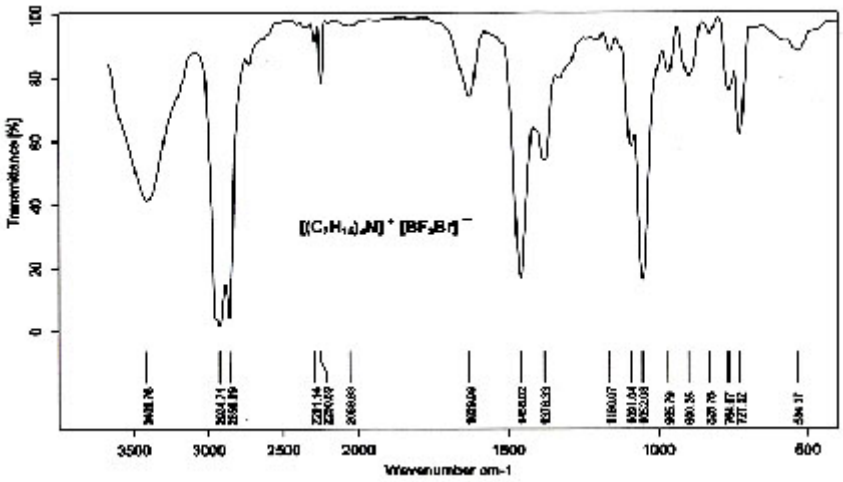

Fig. 1. IR spectrum of $[(C_7H_{15})_4N]^+[AlCl_3Br]^-$

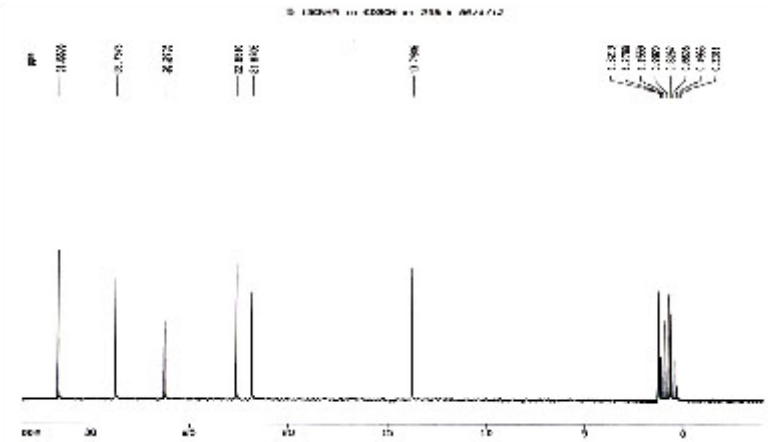

Fig. 2. ^{13}C-NMR Spectrum of $[(C_7H_{15})_4N]^+[AlCl_3Br]^-$

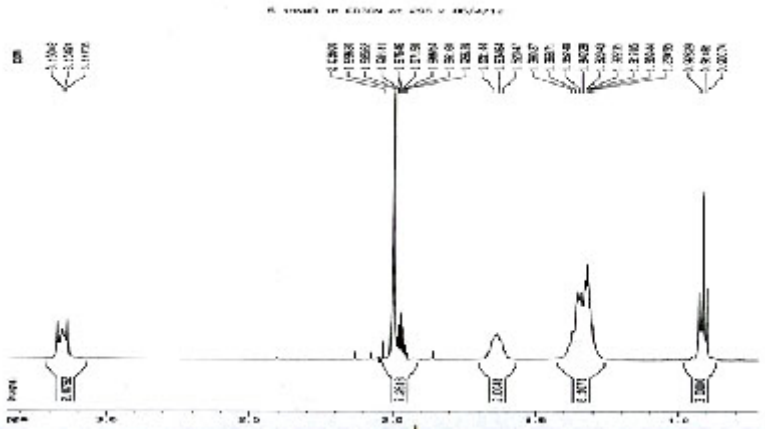

Fig. 3. ^{1}H-NMR Spectrum of $[(C_7H_{15})_4N]^+[AlCl_3Br]^-$

RESULTS & DISCUSSION

The salt/Lewis acid adducts usually result in either ionic liquids or crystalline materials with low melting points. Salts containing large organic cations, such as butylpyridinium chloride or 1,3-dialkylimidazolium chloride, interact with $AlCl_3$ to form ionically conducting liquids at room temperature. Solid $AlCl_3$ has a melting temperature at 193 °C. Upon melting, $AlCl_3$ consists primarily of discrete Al_2Cl_6 dimers, and appears as a molecular liquid with high vapor pressure. It is well known that the melting point of $AlCl_3$ can be lowered upon mixing with RCl (R denotes such as an alkali metal or organic cation), which is believed to originate from the Lewis acid–base interactions of $AlCl_3$ with RCl and the formation of large-sized complex anions, such as $AlCl_4^-$, $Al_2Cl_7^-$ and $Al_3Cl_{10}^-$. From the binary phase diagram, it is found that a low-lying eutectic occurs in the 2:1 composition of $AlCl_3$–RI. Melting temperature of the eutectic is well below that of the $AlCl_3$, representing the minimum liquid us temperature throughout the entire system.

We continue to focus on the synthesis and characterization of various ionic liquids[12–14]. In this

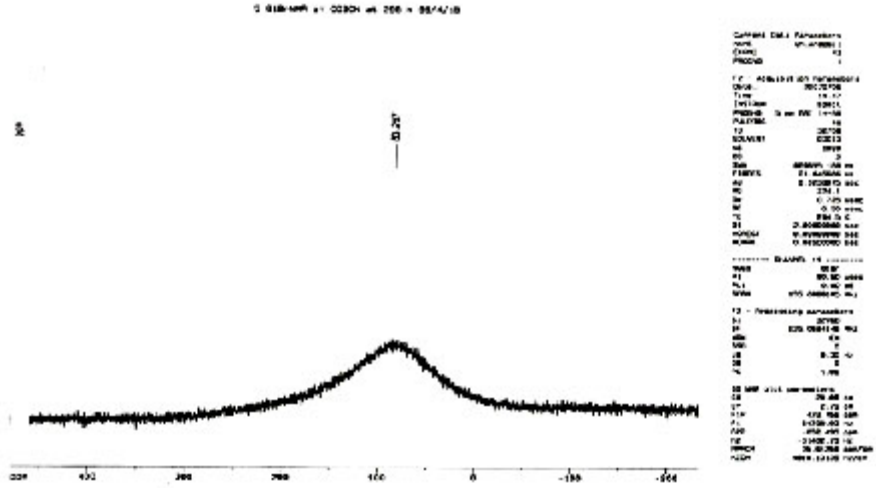

Fig. 4. ^{1}Br-NMR Spectrum of $[(C_7H_{15})_4N]^+[AlCl_3Br]^-$

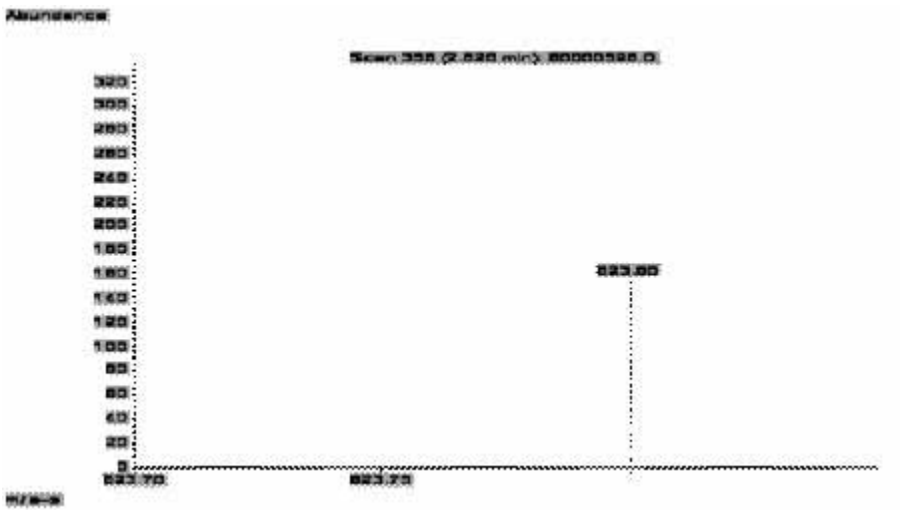

Fig. 5. Maa spectrum of $[(C_7H_{15})_4N]^+[AlCl_3Br]^-$

paper, we report the synthesis of the new ionic liquid containing (bromotrichloroaluminate $[AlCl_3Br]^-$ anion and Tetrahepthylammonium$[(C_7H_{15})_4N]^+$cation). Ionic liquid was synthesized through a one-step reaction. Our procedure for producing ionic liquid has some advantages. For example, there is no side product in preparing ionic liquid in our method, the reaction is quite fast and does not require any severe conditions such as high pressure or high temperature, and it is not sensitive to air. Reporting the synthesis of Tetrahepthylammoniumbromo-trichloroaluminatehas been shown that aluminate was useful for organic chemists. They are analog of the above aluminate compounds.

$$[C_7H_{15})_4N\ Br] + AlCl_3 \rightarrow [(C_7H_{15})_4N]^+[AlCl_3Br]^-$$

After preparing ionic liquid, was characterized by FT-IR, ^{13}C-NMR, ^{1}H-NMR, ^{81}Br-NMR, Mass spectroscopy and other popular experimental methods, and these data have already been mentioned. Moreover, Table 1 lists most important observed vibrational modes of ionic liquid in 400–4000 cm^{-1} range. As shown in Table 1, all reported frequencies corresponding to vibrational mode and the quantity of these frequencies agree with other similar compounds. In most of cases, frequencies in this ionic liquid are nearly the same and the difference between their frequencies is very small. After preparing and characterizing the ionic liquid by experiments, we decided to do some calculations on these molecules. Therefore, we applied the Gaussian program and the molecule was optimized by the DFT method using B3LYP/LANL2DZ basis set.

Then, the infrared spectrum of the new ionic liquid was studied using the same method and basis set. The cations and anions are commonly assumed to be in a hypothetical gaseous free state and without any pre-assumed symmetry, but some calculations also involve better approximations to real systems. After the optimization procedures, giving geometry with a minimum energy –perhaps not a global one the vibrational frequencies and intensities and the eigenvectors for the normal modes are calculated and displayed on a computer screen, to identify the dominating motions.

Mass Spectroscopy shows this IL compound has a peak that related to molecular weight in m/e=455.8 and gives a strong reason for synthesis of the molecule (Fig. 5).

CONCLUSIONS

In this work, a novel aluminate ionic liquid with formula $[(C_7H_{15})_4N]^+[AlCl_3Br]^-$ was synthesized from the reaction of tetrahepthylammoniumbromide with acetonitrile. The structure of compound has been calculated and optimized by the density functional theory (DFT) based method at B3LYP/6-311G levels of theory, using the Gaussian 98 package of programs. The comparison between theory and experiment is made. This compound was characterized by FT-IR, ^{13}C-NMR, ^{1}H-NMR, ^{81}Br-NMR, Mass spectroscopy and other techniques (Figs. 1-5).

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