

2-Acrylamido-2-methyl-1-propane Sulfonic Acid Based Ionic Liquid: Structural and Thermal Characterization

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An ionic liquid (salt structure) was prepared by neutralization of 2-acrylamido-2-methyl-1-propane sulfonic acid (AMPS) with pyridine. The characterization of the salt (AMPS-pyridine) was performed using the Fourier transform infrared spectroscopy, proton nuclear magnetic resonance spectroscopy ($^1\text{H-NMR}$), X-ray diffraction, thermal gravimetric analysis, differential scanning calorimetry, and scanning electron microscopy.

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1. Introduction

Synthesis and characterization of ionic liquids (ILs) have gained growing interest because of their great number of applications such as in chemical synthesis [1, 2], electrochemistry [1, 2], catalysis/biocatalysis [1, 2], CO_2 capture [3], energy storage [2, 3] and magnetic responsive materials [4]. Melting point of these organic/inorganic salts is basically below 100°C [2]. They mainly contain organic cations and inorganic or organic anions [5, 6]. ILs exhibit outstanding properties such as negligible vapor pressure [1, 3, 5], perfect thermal stability [1, 4], chemical stability [1], high conductivity [1, 5, 6] and wide potential/electrochemical window [1, 5, 6]. ILs can be classified into two groups. Conventional or aprotic ILs include organic cations (i.e. imidazolium or pyridinium) and anions (i.e. Cl^- , Br^- , BF_4^- , PF_6^-). However, in general, preparation of protic ILs is based on an acid and an organic base neutralization [7]. It was reported that ILs exhibiting polymerizable character because of the presence of vinyl group on the anions (or the cations) can be used in the synthesis of gels [1].

The aim of the present study is to prepare an ionic liquid (in the solid salt form) by using a strong acidic anionic monomer, AMPS, and an aromatic amine (pyridine), and to perform its detailed characterization by the Fourier transform infrared spectroscopy (FTIR), thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), scanning electron microscopy (SEM) and X-ray diffraction (XRD) techniques.

2. Experimental

2.1. Materials

AMPS was purchased from Merck Schuchardt OHG (Germany). Acetone (Sigma-Aldrich Laborchemikalien GmbH) was used as the solvent. Pyridine was of Sigma-Aldrich (> 99%) product.

2.2. AMPS — pyridine synthesis

AMPS-pyridine salt was synthesized at room temperature using acetone as the solvent. AMPS (10 g) was dispersed in acetone (50 ml), and then predetermined amount of pyridine was added slowly while stirring. Formation of a homogeneous and transparent solution was observed. After evaporation of the solvent, the obtained salt in the form of solid white powder was dried first in air and then in the vacuum oven at 40°C . If ionic liquids are available in the solid form at room temperature unlike their name, they can be called “solid ionic liquids” [3]. Importantly, these type of ILs can be potential alternative to room temperature ILs for CO_2 capture and energy storage [3].

2.3. Characterization study and instrumentation

AMPS-pyridine salt was analyzed by FTIR. FTIR bands were recorded by using the Bruker Vertex 70 FTIR Spectrometer. $^1\text{H-NMR}$ of AMPS-pyridine salt was recorded on a Varian UNITY INOVA 500MHz NMR spectrometer using D_2O as a solvent. DSC analysis of AMPS-pyridine salt was carried out with DSC-60 Shimadzu. The analysis was completed under a scanning rate of $10^\circ\text{C}/\text{min}$, nitrogen gas flow rate of 20 ml/min and temperature range of (-30) – 100°C . The TGA of AMPS-pyridine was conducted using Shimadzu DTG-60 instrument at a $10^\circ\text{C}/\text{min}$ heating rate in a nitrogen atmosphere (20 ml/min) from room temperature to 500°C . X-ray diffraction analysis of AMPS-pyridine was performed with XRD (Rigaku D/Max-2200/PC). Zeiss EVO[®]LS10 instrument was used for SEM analysis of AMPS-pyridine salt.

3. Results and discussion

3.1. FTIR characterization

Structure of AMPS-pyridine salt was analyzed by FTIR technique and corresponding spectrum was shown in Fig. 1. Spectrum of AMPS-pyridine salt includes peaks belong to both AMPS monomer and pyridine. The peaks

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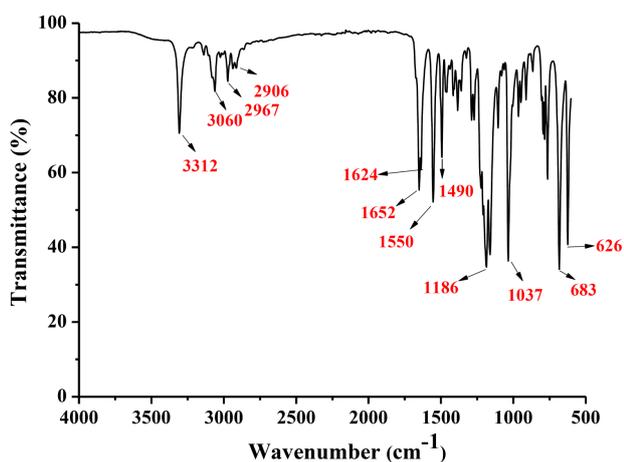


Fig. 1. FTIR spectrum of AMPS-pyridine.

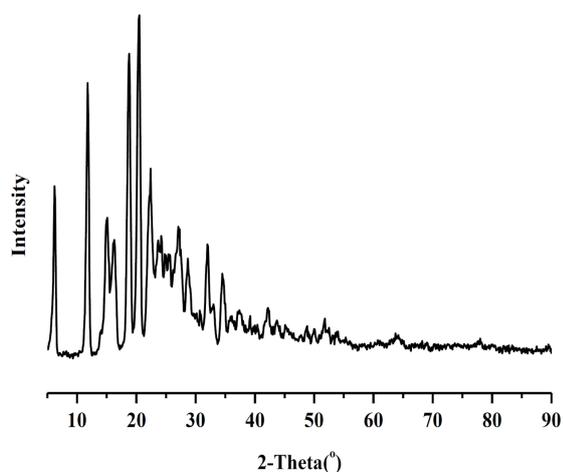


Fig. 2. XRD of AMPS-pyridine.

at 1037 and 1186 cm^{-1} are assignable to the stretching vibrations in sulfonic acid groups, respectively [8–10]. While the peak at 626 cm^{-1} shows the C–S bond absorption [9], –C=C bond is predicted at 1624 cm^{-1} [8, 9]. Amide II band is present at 1550 cm^{-1} [8]. The C–H bond stretching of the aromatic ring is observed at about 3000–3100 cm^{-1} range [11]. The peaks at about 1460 and 1490 cm^{-1} can be related to the pyridine ring [11]. The C=C frequency is seen at 965 cm^{-1} , which is also characteristic for the vinyl monomers [10]. While C=O stretching band is seen at 1652 cm^{-1} [8, 10], the peak at 2967 cm^{-1} can be attributed to OH bond in sulfonic acid [10]. O–H stretching is present in the region 3312 cm^{-1} [8].

3.2. XRD study

XRD analysis on AMPS-pyridine was conducted to investigate its crystallization character. XRD pattern depicts that AMPS-pyridine salt is of crystalline character. Some strong diffraction peaks can be listed as at $2\theta = 20.48^\circ$, 18.79° and 11.80° (Fig. 2).

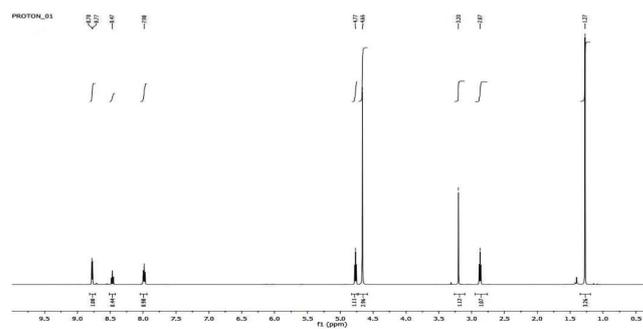
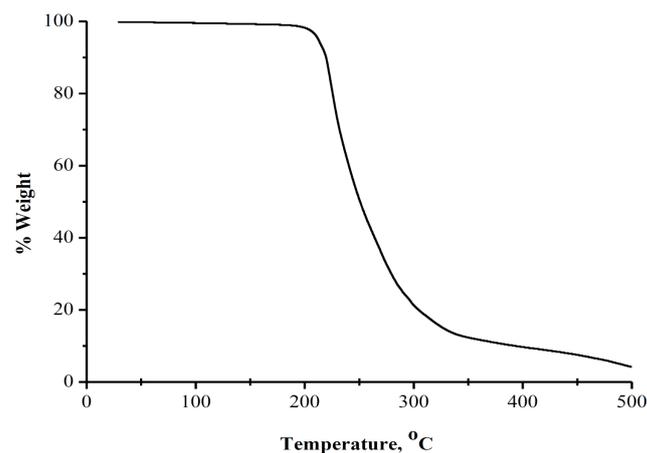
Fig. 3. ^1H -NMR spectrum of AMPS-pyridine (D_2O).

Fig. 4. Thermogravimetric curve of AMPS-pyridine.

3.3. ^1H NMR

Chemical shift values (Fig. 3) confirmed the structure of the resulted salt. In this figure, both AMPS and pyridine chemical shift values are included. Methylene (CH_2) group hydrogens bonded to SO_3H can be seen at 3.20 ppm [8, 10, 12], while the main chain hydrogens signals present at 1.27 and 1.40 ppm [8, 10, 12] and NH hydrogens can be seen at 4.66 ppm [12]. The peaks observed in the region 7.96–8.78 ppm correspond to pyridine [13]. In the pure pyridine spectrum (figure is not given), the signals were observed in the region 7.3–8.61 ppm.

3.4. Thermal behavior

Thermal character of AMPS-pyridine was analyzed by TGA (Fig. 4) and DSC (Fig. 5).

It was reported that $-\text{SO}_3\text{H}$ groups decompose between 250 and 300° [8, 14]. When classic ionic liquids evaluated in terms of thermal stability, their decomposition temperature can vary between 300–400° [15]. The weight loss of AMPS-pyridine was found to be 1.7, 49.3 and 78.7% at 200, 250 and 300°, respectively, which can be assigned to the degradation of $-\text{SO}_3\text{H}$. Weight loss became 90.3% at 400°. Effect of anion can be more dominant than the cation on the thermal stability of ionic liquids [16].

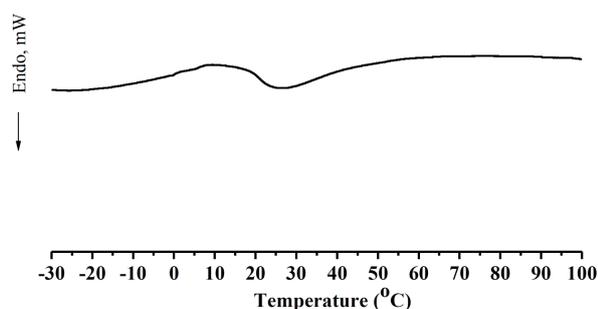


Fig. 5. DSC thermogram of AMPS-pyridine.

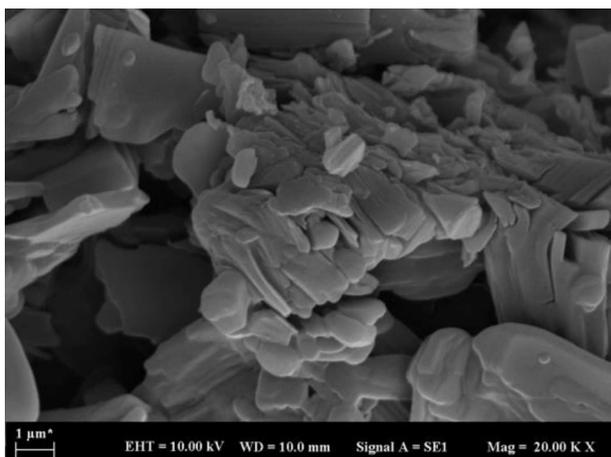


Fig. 6. SEM image of AMPS-pyridine.

In the present study, it can also be concluded that AMPS is more efficient on the thermal behavior. In the DSC thermogram, the observed glass transition of AMPS-pyridine is about 18°.

3.5. SEM

Figure 6 depicts SEM analysis of AMPS-pyridine. Morphology of AMPS-pyridine is compatible with a salt structure.

4. Conclusion

An ionic liquid based on AMPS and pyridine was prepared and a comprehensive characterization study was performed to verify salt structure and to investigate its thermal behavior. Important observation was its solid state at room temperature. This study showed that AMPS-pyridine may have great potential for solid ionic liquid studies.

Acknowledgments

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