

1 IL characterization

The synthesised ILs were characterized by ATR-IR and $^1\text{H-NMR}$, before and after the whole process to evaluate their possible reutilization.

1.1 $[\text{HC}_4\text{im}][\text{HSO}_4]$

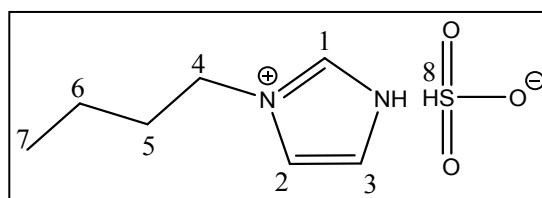


Figure 1: $[\text{HC}_4\text{im}][\text{HSO}_4]$ chemical structure

$[\text{HC}_4\text{im}][\text{HSO}_4]$ was prepared by the direct combination of 1-butylimidazole and H_2SO_4 . During the $[\text{HC}_4\text{im}][\text{HSO}_4]$ synthesis special attention was paid to maintaining the 1:1 ratio of the reactants, so the H_2SO_4 was titrated before use. The reaction was cooled in a dry ice bath, due to the highly exothermic reaction. The $[\text{HC}_4\text{im}][\text{HSO}_4]$ was dried for several hours under vacuum reaching a moisture content of 2%. The $[\text{HC}_4\text{im}][\text{HSO}_4]$ is a salmon liquid at room temperature. It was characterized by $^1\text{H-NMR}$ and ATR-IR.

Figure 2 shows the spectra of the freshly prepared $[\text{HC}_4\text{im}][\text{HSO}_4]$ and after the treatment with the different concentrations of H_2O_2 . The spectral bands of the pure $[\text{HC}_4\text{im}][\text{HSO}_4]$ were assigned as follows (Fig. 1): 0.88 (m) CH_3 (7), 1.22 (m) ppm CH_2 (6), 1.76 (pt) ppm (q) CH_2 (5), 2.51 ppm (dt) DMSO, 4.21 ppm (t) CH_2 (4), 7.65 ppm (t) CH (2), 7.79 ppm (t) CH (3), 9.11 ppm (t) CH (1) and 11.57 ppm HSO_4 (8). After oxidation treatments it was observed that the IL was oxidizing and the oxidation was higher with the increase of concentration of H_2O_2 , a band assigned to acidic water was displaced from 9.5 to 10 and other small bands appeared at higher displacements, due to the OH groups formed by the oxidation.

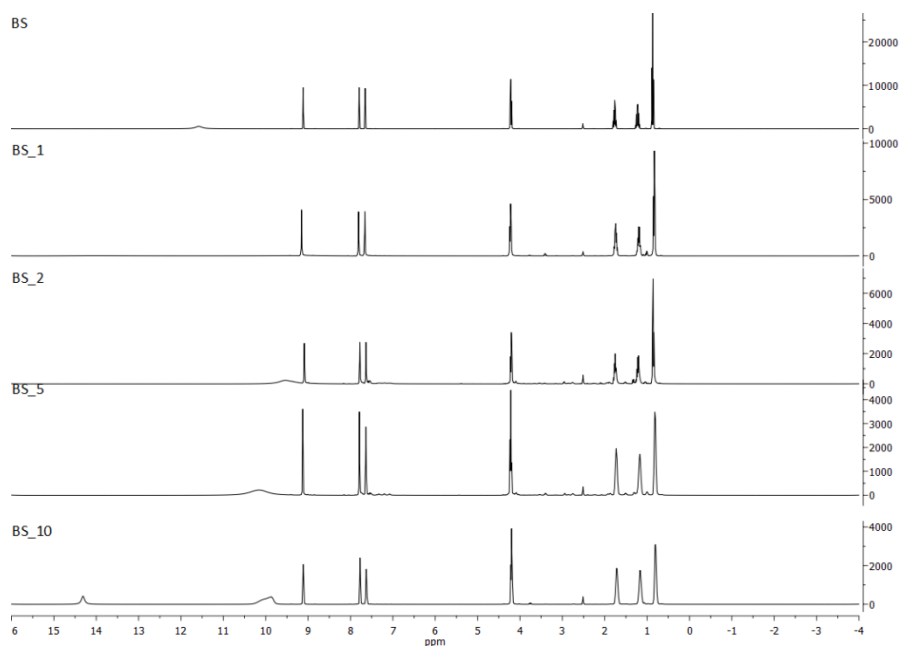


Figure 2: ¹H-NMR of [HC₄im][HSO₄]

Figure 3 shows ATR-IR spectra of [HC₄im][HSO₄] before and after the treatment. The bands were assigned as follows to the pure [HC₄im][HSO₄]: bands at 3138 and 3065 cm⁻¹ were assigned to asymmetric and symmetric stretching vibrations of CH in the imidazolium ring, bands at 2962, 2935 and 2874 cm⁻¹ were assigned to stretching vibration of CH₂ and CH₃ in butyl chain, bands at 1580, 1548 and 1514 cm⁻¹ were assigned to C-C and C-N vibrations of the ring, the band at 1463 cm⁻¹ was assigned to NH deformation vibration, bands at 1408, 1159 and 1028 cm⁻¹ were assigned to HOSO₃⁻ stretching vibrations, the band at 1087 cm⁻¹ was assigned to the plane wagging vibration of the alkyl chain with the ring, and the band at 838 cm⁻¹ was assigned to CH in-plane vibration.

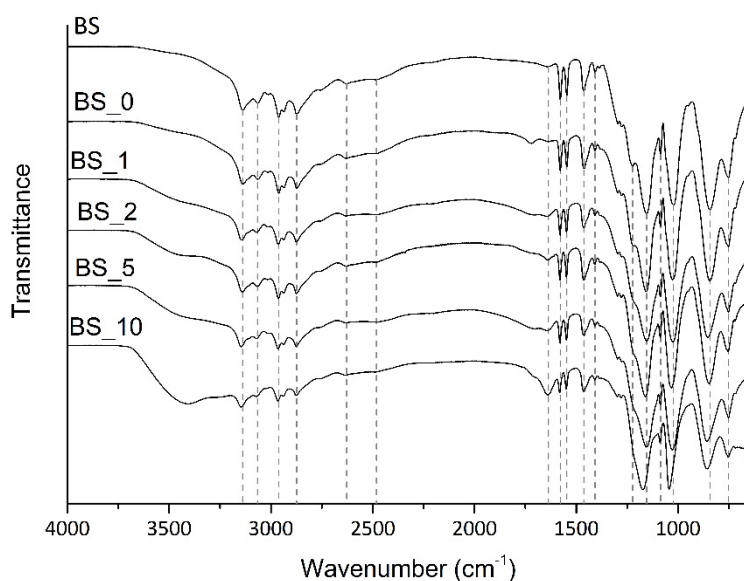


Figure 3: ATR-IR spectrum of BHimHSO₄

1.2 [Et₃NH][HSO₄]

[Et₃NH][HSO₄] was prepared by the direct combination of triethylamine and H₂SO₄. During [Et₃NH][HSO₄] synthesis special attention was paid to maintaining the 1:1 ratio of the reactants, so the H₂SO₄ was titrated before use and it has to be 5M to avoid solidification. The resultant ionic liquid was dried under vacuum for several hours until the moisture content was lower than 2%. The appearance of the ionic liquid was a white solid at room temperature. It was characterized by ¹H-NMR and ATR-IR.

The ¹H-NMR spectrum did not show any impurity (Fig. 4), bands were assigned as follows: 1.18 ppm (t) CH₃, 3.06 (q) ppm CH₂, 2.51 ppm (dt) DMSO, and 9.41 ppm (s) HSO₄, there was no evidence of new bands after oxidation treatment.

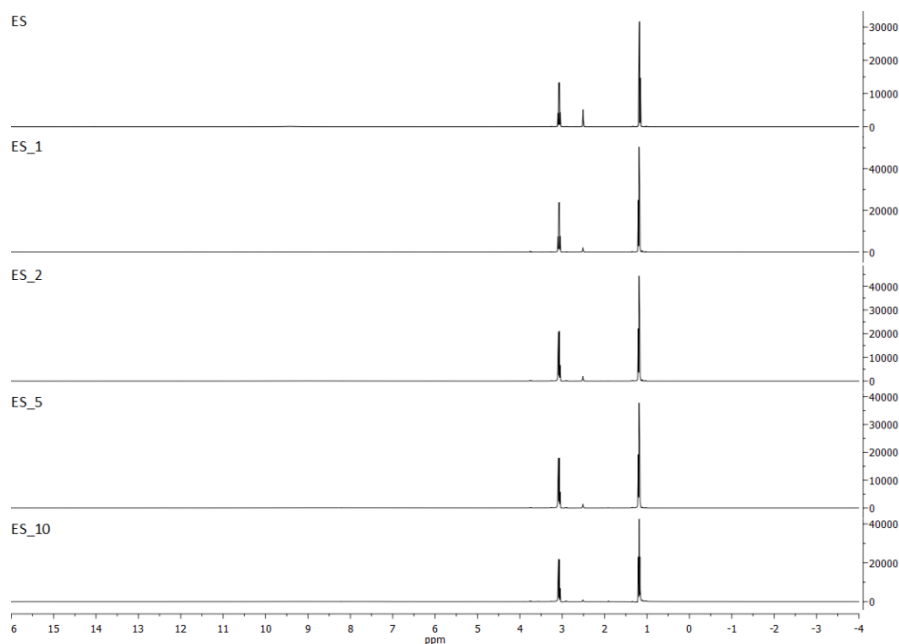


Figure 4: $^1\text{H-NMR}$ 22 h pretreatment $[\text{Et}_3\text{NH}][\text{HSO}_4]$ after H_2O_2 treatment

Figure 5 shows the ATR-IR spectra of $[\text{Et}_3\text{NH}][\text{HSO}_4]$ before and after the treatment. All spectra showed the same main bands, that were assigned as follows; bands at 3138 and 3065 cm^{-1} were assigned to asymmetric and symmetric stretching vibrations of CH in the imidazolium ring, bands at 2962 , 2935 and 2874 cm^{-1} were assigned to stretching vibration of CH_2 and CH_3 in butyl chain, bands at 1580 , 1548 and 1514 cm^{-1} were assigned to C-C and C-N vibrations of the ring, the band at 1463 cm^{-1} was assigned to NH deformation vibration, bands at 1408 , 1159 and 1028 cm^{-1} were assigned to HOSO_3^- stretching vibrations, the band at 1087 cm^{-1} was assigned to the plane wagging vibration of the alkyl chain with the ring, and the band at 838 cm^{-1} was assigned to CH in plane vibration. For spectra after pretreatment and treatment the same impurities bands were observed, those new bands were assigned as follows; at 1737 and 1647 cm^{-1} which were assigned to absorption of moisture and 1217 cm^{-1} assigned to CH and OH groups deformation, it seemed that after treatment the only impurity was the presence of water.

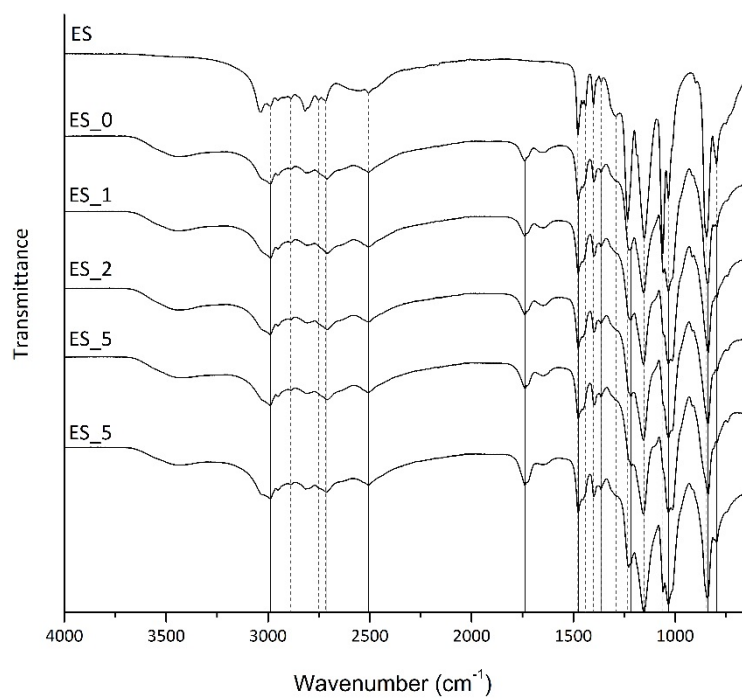


Figure 5: ATR-IR spectra of $[\text{Et}_3\text{NH}][\text{HSO}_4]$ after treatment with H_2O_2 and pretreatment