Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Insights on the catalytic behaviour of sulfonic acid-functionalized ionic liquids (ILs) in transesterification reactions – Voltammetric characterization of sulfonic task-specific ILs with bisulfate anions

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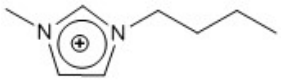
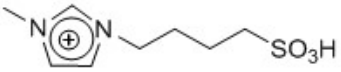
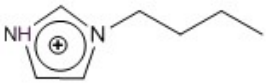
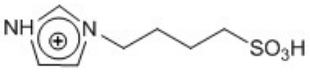
S1. Cationic bases of the analyzed ionic liquids (ILs)

Four ILs with bisulfate counterion and imidazolic bases whose structures are listed in Table S1 were synthesized and evaluated.

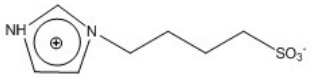
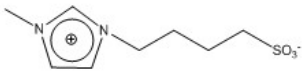
Table S1. Cationic base structures of the analyzed ILs with bisulfate counterion

Imidazolium-based cation	Acronyms
 *1-butyl-3- methyl-imidazolium*	bmim
 *1-(4-sulfonic acid)-butyl-3-methylimidazolium*	bsmim
 *1-butyl-imidazolium*	bHim
 *1-(4-sulfonic acid)-butyl-imidazolium*	bsHim

S2. Imidazolic zwitterions used for synthesis of sulfonic-acid functionalized ILs

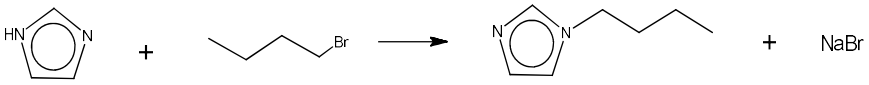
The sulfonic-acid funcionalized ILs [bsmim]HSO_4 and [bsHim]HSO_4 were synthesized by reaction of sulfuric acid with the corresponding zwitterions, which are listed in Table S2.

Table S2. Structures of the imidazolic zwitterions used for synthesis of sulfonic TSILs

Imidazolic zwitterions	Acronyms
 *4-(1-methylimidazolium-3-yl)-1-butane sulfonate*	ZbsHim
 *4-(1-imidazolium-1-yl)-1-butane sulfonate*	Zbsmim

S3. Details on the synthesis of 1-butyl-imidazole (bim)

1-butyl-imidazole (bim) was synthesized by reaction of imidazole with butyl bromide through reaction (S1).



(S1)

Briefly, 0.05 mol of imidazole dissolved in 20 ml of ethanol (EtOH) were placed in a two-neck round bottom flask, and 0.055 mol of sodium ethoxide were added dropwise under stirring with a magnetic bar for 1 h. After this period, 0.055 mol of butyl bromide were slowly added for 1 h and let to react at room temperature (RT) for 30 min. The obtained solution was filtered and evaporated under vacuum at 80°C for 1 h. The mixture was finally vacuum distilled at 20 mbar and 118°C.

S4. Results from the voltammetric analysis of $[bHim]HSO_4$

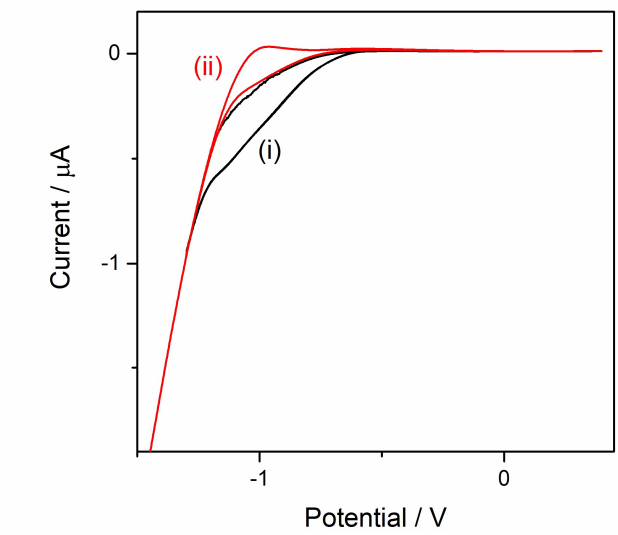


Figure S1. CVs of a Pt ME in $[bHim]HSO_4$ at 80°C before (i) and after (ii) addition of pure bim. T = 80°C; v = 0.1 V s^{-1}.

S5. Details on the processing of UV-vis spectra for measuring of peak absorbances

For measuring the absorbance of the peak corresponding to *p*-nitrophenol (PNP) at λ = 310 nm, first a baseline was subtracted. When both PNP and *p*-nitrophenyl acetate (PNPA) were present, a deconvolution process of both detected peaks was applied. Then the absorbance was measured at the maximum of the peak located at λ = 310 ± 5 nm. The whole treatment is exemplified in Fig. S2.

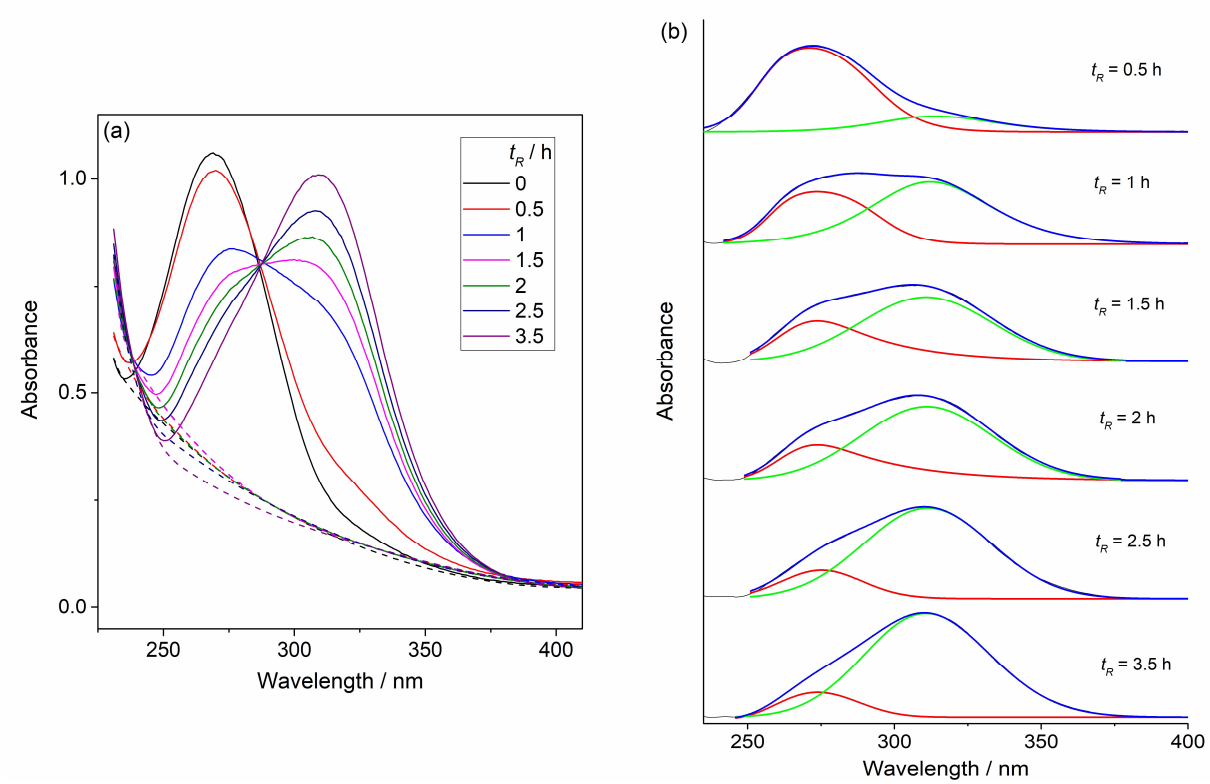


Figure S2. Processing of UV-vis spectra acquired on the reaction media for the transesterification reaction of PNPA with MeOH leading to PNP at 25°C in the presence of H_2SO_4, acquired at different reaction times (t_R) as indicated in each graph.(a) Raw spectra (solid lines) and respective baselines (dashed lines).(b) Spectra after baseline subtraction (black lines) and fitted curves (blue lines) with deconvoluted peaks for PNPA (red lines) and PNP (green lines).

S6. Calibration curves for estimation of PNP concentrations from UV-vis spectra

As it was described, the PNP concentrations (C_{PNP}) were estimated using these UV-vis spectra taken at different t_R values from the absorbances of the peak measured at λ = 310 ± 5 nm, and using calibration curves measured on standard solutions of PNP in MeOH containing the respective IL (or H_2SO_4). The UV-vis spectra acquired on standard solutions of PNP in MeOH with the different ionic liquids (or H_2SO_4) and the respective calibration curves are shown in Fig. S3.

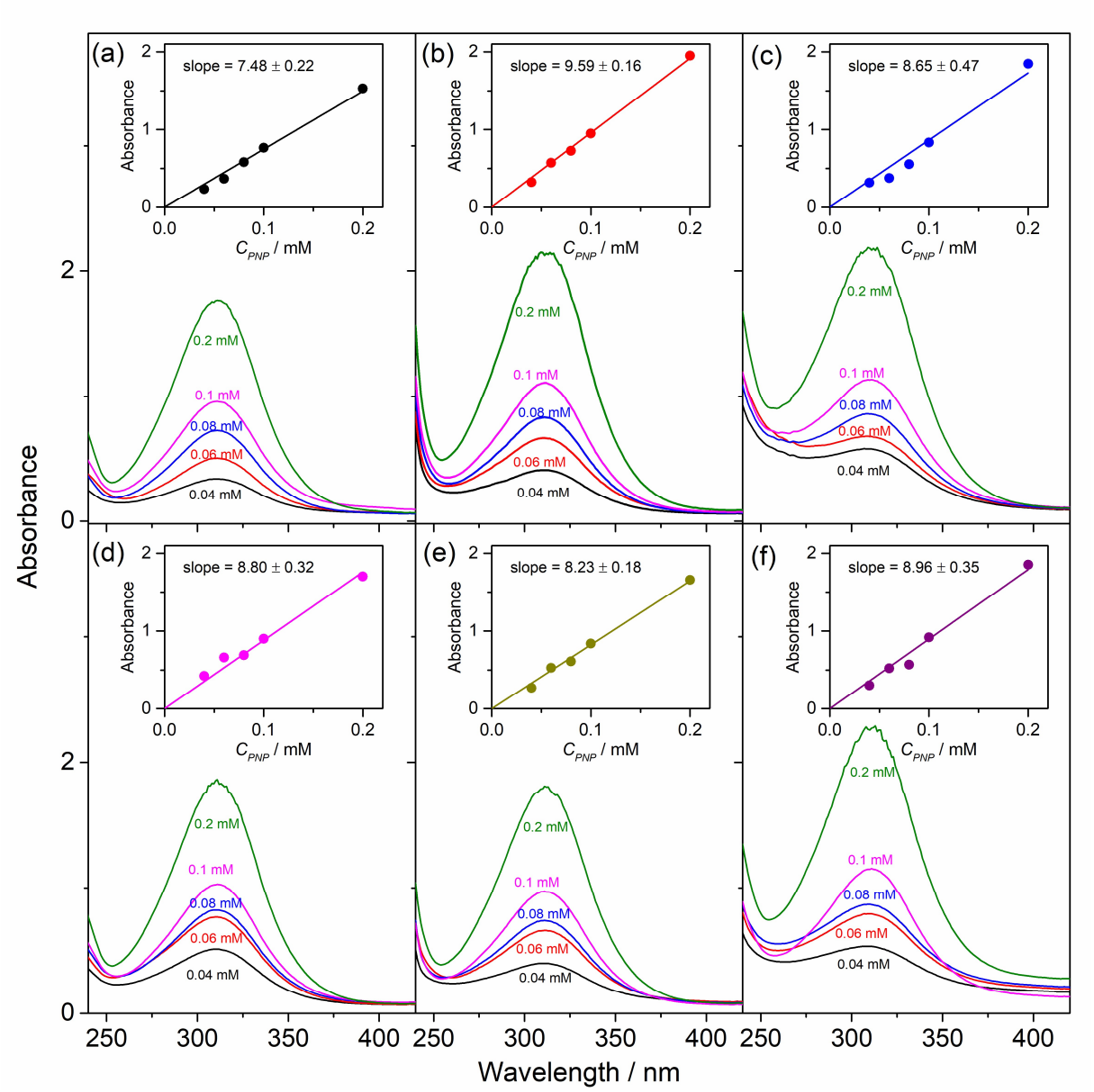


Figure S3. UV-vis spectra acquired on standard solutions of PNP in MeOH with concentrations indicated within the graphs, and containing the different catalysts that were tested in the transesterification reaction: none (a); [bmim]HSO_4 (b); [bHim]HSO_4 (c); H_2SO_4 (d); [bsmim]HSO_4 (e); [bsHim]HSO_4 (f). The respective calibration curves are shown in the inset graphs.

S7. UV-vis spectra measured at different reaction times used for calculation of reaction yields plotted in Figure 6

UV-vis spectra were recorded at different t_R values on the reaction media when using as catalysts both crude [bsmim]HSO_4 (without purification steps) containing a significant excess of free H_2SO_4 as noted by the CV in Fig. 2b(i), and [bsmim]HSO_4 that received the addition of Zbsmim (54 mg) for neutralizing the excess of free H_2SO_4 down to the minimum concentration in equilibrium with saturated Zbsmim, as verified by the CV in Fig. 2b(iv). These spectra are shown in Fig. S4.

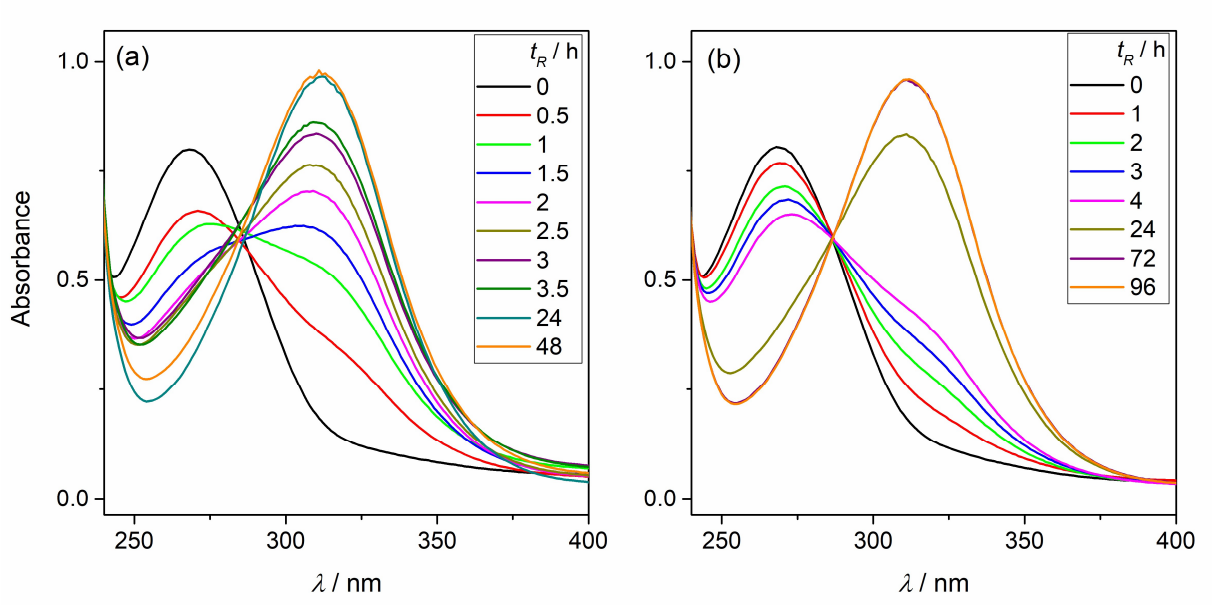
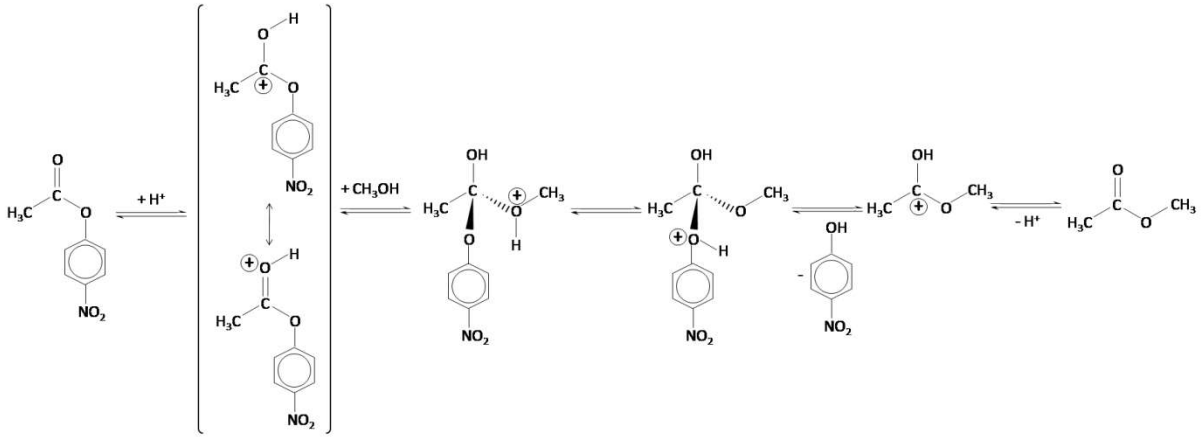


Figure S4. UV-vis spectra of the reaction media for the transesterification reaction of PNPA with MeOH at 25 °C in the presence of crude [bsmim]HSO_4 (a) and [bsHim]HSO_4 with three successive additions of Zbsmim (54 mg total) (b), acquired at different t_R values as indicated in each graph.

S8. Potential mechanisms for the transesterification of PNPA with MeOH

The mechanisms of transesterification reactions have been the subject of numerous investigations for more than sixty years,[1] and are described in basic textbooks on Organic Chemistry. With the renewed interest in biodiesel, this reaction has regained importance,[2] and new studies have been recently reported that incorporate mechanistic analysis by molecular modeling.[3-6] Even though the mechanism may vary depending on the chemical structure of the ester and on the steric impediments of the formed intermediate, the most accepted pathway for a general transesterification reaction with primary and secondary alcohols is sketched in Scheme S1 for this particular reaction. It involves the ester protonation and further nucleophilic addition of MeOH to the carbonyl carbon leading to a tetrahedral intermediate. The last steps involve the acyl C–O bond cleavage of the intermediate and consequent elimination of PNP.



Scheme S1. Possible mechanism for the transesterification of PNPA with MeOH (adapted from most accepted pathways proposed in refs. [3-6])

When using protic ILs and TSILs as acid catalysts, the required protons could be provided by different sources located both within the molecular structures of the ionic pairs (such as the SO_3H group in TSILs, the imidazolic hydrogen, and the bisulfate counterion) and at the free species (such as sulfuric acid) that remain in autoprotolysis equilibrium with the ionic pair.

S8. Calculation of apparent pseudo-first-order kinetic constants for the transesterification reaction

It is usually accepted that the first protonation step is fast, so it can be considered always in equilibrium, and that the rate-determining step is the slow nucleophilic addition of MeOH to the protonated carbonyl group. Thus, if the reaction is considered irreversible, and as it proceeds with an excess of methanol, the reaction rate (r) should be properly described by a first order dependence on PNPA concentration. Thus, taking into account that $r = -dC_{PNPA}/dt = k^{app}C_{PNPA}$ (where k^{app} is the apparent pseudo-first-order kinetic constant) the variation of the reaction conversion (X = yield/100) on time that results from integrating the previous dependence is given by eq. (S2).[2,7]

$$\ln(1 - X) = -k^{app}t \qquad \text{(S2)}$$

As the X values can be calculated from the yields plotted in Figs. 6 and 7, the k^{app} values can be obtained from the slopes of the linear fittings of the -ln(1-X) vs. t dependences, which are shown in Fig. S5.

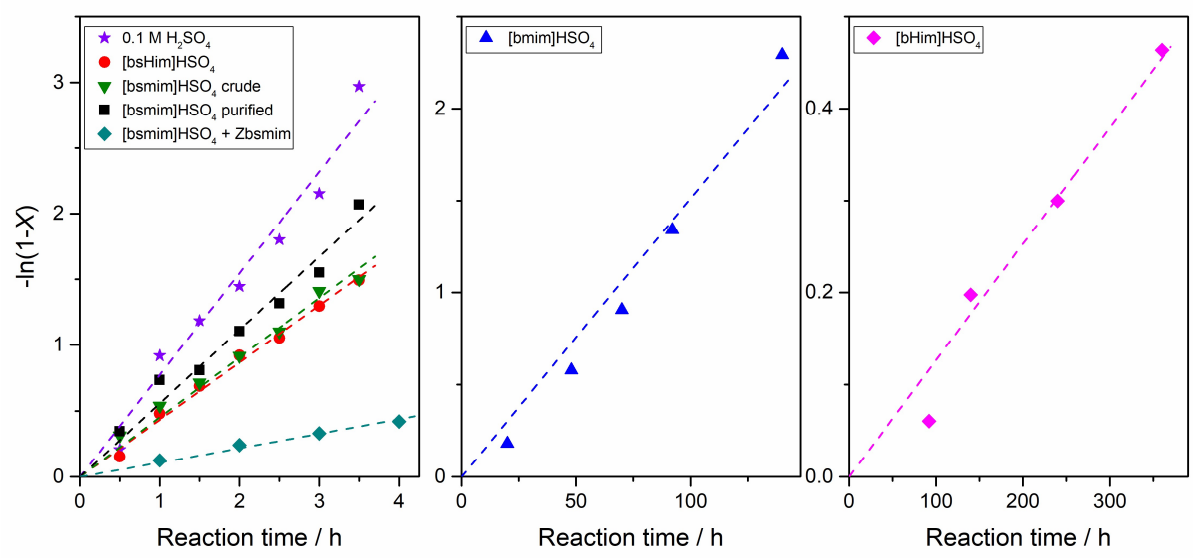


Figure S5. Dependences of the reaction conversion (X) on time for the transesterification reaction of PNPA with an excess of MeOH at 25 °C in the presence of the different acid catalysts indicated in each graph. Dashed lines indicate the linear fittings of the –ln(1-X) vs. t dependences.

S9. References

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