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Comment on 'Chitosan dissolution with sulfopropyl imidazolium Brønsted acidic ionic liquids'

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Abstract. This comment identifies misinterpreted data associated with a reported synthesis of Brønsted acidic ionic liquids 1-alkyl-3-(3-sulfopropyl)imidazolium acetate for the dissolution of chitosan. Relying on the Brønsted-Lowry theory, NMR analyses, and density functional calculations, we demonstrate that such ionic liquids are unlikely to be produced.

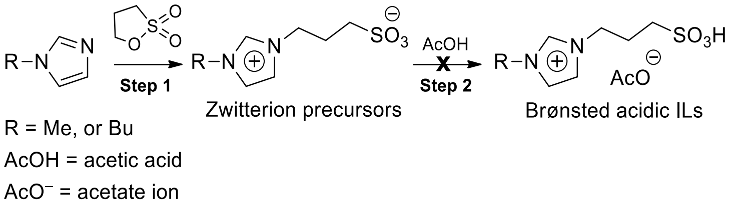
Keywords: Brønsted acidity, ionic liquids, carbohydrate polymers, sustainable chemistry

Highlights

- Errors found in the reported synthesis of Brønsted acidic ionic liquids.
- Interpretation of NMR spectra is provided.
- Molecular modelling of the reported ionic solvents presents their actual structures.

The article 'Chitosan dissolution with sulfopropyl imidazolium Brønsted acidic ionic liquids' [1], published in *this journal*, investigates the use of acidic ionic solvents as more sustainable media for the dissolution of chitosan. The scope of the reported work is highly relevant for the areas of sustainable industrial chemistry, given the low toxicity and tunability (i.e. ease of access of the systems with specific chemical and physical characteristics) of many ionic liquids (ILs), along with their special abilities to solubilise varied carbohydrate polymers for processing, such as shaping into fibrous materials, or chemical conversion into value added derivative products [2–4]. However, the interpretation of the scientific data that are presented in the article [1] warrant a correction to avoid similar faults in future studies. Here, we conduct a critical overview of key aspects of the published results, with an emphasis on the synthesis, structural characterisation and the acidity of the prepared solvents. While there are numerous other errors in the paper [1], we focus on those of greatest substance.

The authors [1] claim the production of the purported acidic ILs, named as mPSAc (1-methyl-3-(3-sulfopropyl)imidazolium acetate) and bPSAc (1-butyl-3-(3-sulfopropyl)imidazolium acetate), in two steps according to references [5–7], as pictorially represented in Scheme 1 (we have inserted the cross over the Step 2 reaction arrow). It is important to note that the cited works [5–7] employ strong acids with which to prepare the acidified sulfonic acids from the parent zwitterions, after the reaction in Step 1. In contrast, in the paper [1], an excess of the weak acetic acid is used (3 eq. of AcOH based on the zwitterion precursor (3-(3-methyl-1-imidazolium)propanesulfonate, or 3-(3-*n*-butyl-1-imidazolium)propanesulfonate)). The pK_a of alkyl sulfonic acids is expected to be < -2, while the pK_a of AcOH is 4.8 (water, 25 °C) [5,8]. It is not expected that AcOH will protonate the sulfonate to any significant extent beyond minimum amounts consistent with equilibrium constants. While there may be subtleties to the Brønsted-Lowry theory in ionic liquid systems, the general principles will still pertain. The seminal study of Davis and colleagues [5], showing the production of sulfonic acid-bearing ILs, exemplifies this point when they employ trifluoromethanesulfonic acid and *p*-toluenesulfonic acid to protonate the zwitterion sulfonate precursors, as do a multitude of subsequent studies. Therefore, given the very significant pK_a difference between acetate anion (or acetic acid) and sulfonic acids, the proposed course of the reaction towards mPSAc and bPSAc cannot be correct (Scheme 1). It is nevertheless possible that the precursor zwitterionic ILs become associated with added AcOH through a hydrogen bond network, rather than by the generation of acidified ILs. This brings the assumptions, interpretations and conclusions of the paper into question, and requiring reinterpretation.



Scheme 1. Proposed 'production' of Brønsted acidic ionic liquids [1]. Reaction conditions: 1-methylimidazole (0.1 mol), 1,3-propanesultone (0.105 mol), dichloromethane (80 mL), from ice bath

temperature to 25 °C, 2 h (at 25 °C), then recovery of zwitterion precursor, and addition of AcOH (3 eq., based on zwitterion precursor), 25 °C, 4h.

The NMR spectra of mPSAc, bPSAc and their respective parent zwitterions are virtually identical with no practical difference at all between them, except that there is a signal for the acetic acid in relevant instances [1]. The most considerable change in chemical shift of any signal is only 0.02 ppm, which is well within experimental error for repeat NMR studies of identical molecules. If it was argued that one mole of acetic acid had protonated the IL, it would form 1 mole of the sulfonic acid, along with 1 mole of AcO^- and leave 2 moles of unreacted AcOH. This would be evident in the NMR spectra; however, it is not. Instead, a 9H singlet is reported for 'acetate ion', and signals associated with the imidazolium systems and their side chains are essentially identical pre- and post-treatment with the AcOH. Even if it was further argued and accepted that proton exchange between AcO^- and AcOH is rapid enough for effective coalescence (this hydrogen bond exchange is usually not visible on the ^1H NMR time scale for AcO^-/AcOH systems in solution, even at low temperatures of 110–150 K [9]), there would be changes to the chemical shifts in the signals associated with the alkyl sulfonate / alkyl sulfonic acid; no such changes are evident. The NMR data thus provide supporting evidence that there were no chemical reactions yielding targeted mPSAc and bPSAc, but do not rule out potential intermolecular binding between the parent zwitterion and AcOH.

To underpin our suspicions, we performed a density functional study using a similar level of theory (B3LYP/6-31g(d,p)) and software [10] to those employed in the work [1]. We found that the Gibbs free energy of formation (ΔG) of mPSAc from the zwitterion precursor and AcOH is too high to accept that this reaction can take place under the specified reaction parameters ($\Delta G = 476.85$ kJ mol^{-1} at 25 °C, Figure 1). These data support the notion that it is unlikely that the proposed Brønsted acidic ILs can be thermodynamic products of the process given in Scheme 1. What we found is that the intermolecular interaction between the parent zwitterion and AcOH can lead to overall stabilisation of the system though the hydrogen bonding ($\Delta G = -30.62$ kJ mol^{-1}, Figure 1). Interestingly, the authors' theoretical study identified similar hydrogen bonding, with only minor structural perturbations compared to our observations (Figure 5 in the article [1]). However, neither our computation nor the reported results suggest that acetic acid can acidify the zwitterion precursors. At the energy minimum of the complex, the bond length of AcO–H remains at approximately 1 Å, which is a bond distance consistent with X–H σ-bonds (X = heteroatom). The –S(O)O···H bond length is significantly longer (1.6 Å), correlating more closely with the ranges reported for hydrogen bonds [11]. Our theoretical study also demonstrates that sulfonate can coordinate up to 3 molecules of AcOH with even greater stabilisation effects, as we judged by the reduced ΔG value ($\Delta G = -42.90$ kJ mol^{-1}, Figure 1).

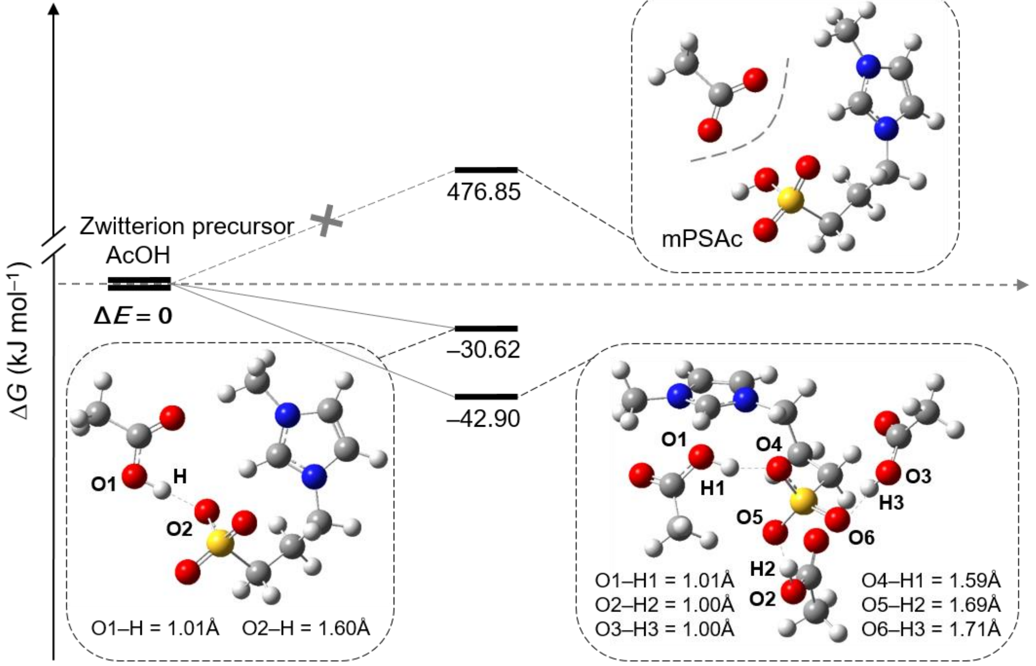


Figure 1. Proposed hydrogen bonding between the zwitterion precursor and acetic acid. Geometry optimisation and calculation of thermodynamic values were performed at B3LYP/6-31g(d,p) level of theory. Δ*G* = Gibbs free energy of formation. Colour of atoms: ● = hydrogen, ● = carbon, ● = nitrogen, ● = oxygen, ● = sulfur.

pH measurements are widely employed and accepted as a technique to determine the activity of hydrogen ions ($H^+(H_2O)_n$, where *n* is an integer and depends on the concentration of the acid [12]) in protic media. This technique can be used to determine the degree of ionisation of an acid as a proxy for its acid strength. In the present instance, it is not possible to quantitatively compare the acidity of the different ILs because the authors employed weight fractions thereof (5% *w/w* aqueous solution), given their differing molar mass, rather than unified concentrations. Nevertheless, the pH readings presented in Table 1 (Table 2 in the original [1]) clearly evidence a set of similar pH readings that are inconsistent with the notion of the formation of sulfonic acid systems in the cases of mPSAc and bPSAc, which are anticipated to give somewhat lower pH readings than presented in the Table. Anomalously, the purported bPSAc system is shown to be *less acidic* than its parent zwitterion. For comparison purposes, sulfuric acid gives pH values <2 for concentrations above about 0.5 g.L^{-1} (pH *ca*. 1.8, 1.7 and 1.4 for a 0.5 wt%, 1.0 wt% and 2.0 wt% aqueous solution, respectively) [13].

Relating to the studies on acidity in the paper, we wish to emphasise alternative and more widely accepted methods than the methodology adopted in the study [1] to rank the acidity of the ionic systems. To avoid issues with indirect methods, such as the solubility or stability of the ILs in water, we recommend employing ^{13}C NMR spectroscopy methods, which are based on the protonation of specific probe molecules with ILs [14]. For example, mesityl oxide is known to form complexes with protic acids, which binding strength correlates to a difference between the chemical shifts of the α and β carbons of the unsaturated ketone, providing a measure of acidity (more significant difference between chemical shifts corresponds to stronger acidity) [14,15]. This method has been previously validated for ILs by Welton and colleagues [14], and has been effectively employed for various classes of ionic solvents [16–18].

Table 1. pH readings of ILs and IL-acetic acid mixtures, 5% *w/w* aqueous solution

Component	pH
Acetate acid	2.39
$mPSO_3$	2.33
$bPSO_3$	2.50
mPSAc	2.03
bPSAc	2.56

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