4-Imidazol-1-yl-butane-1-sulfonic acid or a novel liquid salt? The NMR analysis and dual solvent-catalytic efficiency for one-pot synthesis of xanthenes

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The reaction of the equimolar mixture of imidazole and 1,4-butane sultone was performed at 90 °C in ethylbenzene for 12 h, and the structure of the product was investigated by the NMR analysis in CD_{3}OD and DMSO-d_{6}. This work demonstrated that 4-imidazol-1-yl-butane-1-sulfonic acid could not be obtained through the above reaction and the mixture of zwitterionic (I) and ionic (II) structure is produced. The structure of the liquid salt (I + II) was characterized and analyzed by 2D NMR. Then, the dual solvent-catalytic efficiency of the liquid salt (I + II) was studied for the synthesis of a variety of xanthenes under mild conditions which afforded the desired products in good to excellent yields within short reaction times. The recyclability of the liquid salt (I + II) was studied with an average recovered yield of 85% for three subsequent runs. The recycled liquid salt showed no significant loss of the catalytic activity even after three runs and its structure remain same as fresh liquid salt (I + II).

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1. Introduction

Ionic liquids (ILs) are widely utilized in the multicomponent reactions as the solvent, catalyst or dual solvent-catalyst owing to eco-friendly properties including low vapor pressure, thermal and chemical stability, high ionic conductivity, tunable polarity and designable properties, simple separation of products and potential reusability [1–9]. The organic products and the ionic liquids can often be separated in the different phases which will make simpler the work-up step and minimizes the consumption of toxic, volatile and flammable organic solvents and avoids tedious separation and purification technology [10,11].

The natural and synthetic xanthene and benzoxanthene derivatives are well-known owing to potential biological and pharmaceutical activities [12–18]. Xanthene dyes are also broadly utilized as sensor probes for visualization of biomolecules [19–21]. In this context, numerous protocols have been reported for the synthesis of xanthene derivatives in the literature [22–32]. Xanthenes are often prepared based on the three-component condensation in the presence of a Lewis or Brönsted acid. Some drawbacks of Lewis acids include their decomposition or deactivation in the presence of moisture, and they often are not technically recoverable or reusable; as well as the residues of Lewis acid can cause the environmental concerns [33]. Some other methods have certain disadvantages such as the low reaction rate and yield, by-product formation, tedious workup, corrosion effects, metal-waste, and acid pollution, and use of expensive catalysts or catalysts containing metals/transition metals, an excess of reagents/catalysts, toxic and flammable organic solvents. Therefore, the design and development of a safer, more convenient and sustainable protocol for the synthesis of xanthenes is highly demanded.

In continue of our interesting to the synthesis of new ILs [34–39], herein, we described our results on the structure elucidation of the obtained product of the equimolar reaction of imidazole and 4,4-butane sultone using the correlation spectroscopy (COSY) and heteronuclear multiple bond correlation (HMBC) experiments. The results displayed the impact of the 1^H,1^H-COSY, 1^H,13^C- and 1^H,15^N HMBC correlations for the preservation or elimination of some structures. Also, the dual solvent-catalytic efficiency of new liquid salt was investigated for the synthesis of symmetric and asymmetric xanthenes under mild conditions.

2. Results and discussion

2.1. Synthesis of the liquid salt (I + II) and the characterization of its structure

The equimolar reaction of imidazole and 1,4-butane sultone in dry ethyl benzene provided a new liquid salt containing zwitterionic and ionic structure viz. 4-[3-(4-sulfo-butyl)-imidazol-1-yl]-butane-1-sulfonate (I) and 4-imidazol-1-yl-butane-1-sulfonate imidazolium (II) in good yield (84%), respectively (Scheme 1).