

SUPPORTING INFORMATION for

High conductivity, and “dry” proton motion, in guanidinium salt melts and their binary solutions

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The material relating to synthesis and characterization of the salts of guanidinium cation prepared for this study, have been rather briefly reported in the manuscript of the above paper. Here we provide details of possible value for those who might wish to duplicate or check this work.

General note: The reactions used in many of the following preparations produce water, so the question of water content of the final product must be addressed. Many ionic liquids are very susceptible to water contamination, and their properties are strongly affected by small amounts of water. Hygroscopicity reflects the competition between lattice energy and hydration energy. The very low melting points of many ionic liquids reflect the weakness of the ionic packing and accordingly points to their low lattice energies. The salts of guanidinium cation, however, are without exception melting at rather high temperatures, none in our experience falling below ambient temperature and most of them falling above 100°C. Evidently the high symmetry of the guanidinium cation leads to relatively high lattice energies. Thus it is not surprising that only in the lowest melting cases were the guanidinium salts found to be hygroscopic. Thus GdmFm, which was observed to be hygroscopic, and was an important component of the only binary system with glassforming ability in this study, was kept in a dessicator, as were all other salts of lower melting point. Mixtures of salts for phase diagram studies, and studies of physical properties over wider temperature ranges, were always prepared in the drybox. And protected from water ingress during measurement.

Because of the high pK_a of guanidine, the proton transfer energy from even the weaker acids of this series of preparations, was quite large, so the risk of composition change due to back reaction and consequent loss of higher vapor pressure components was small. Accordingly, removal of water by vacuum drying was a viable procedure, though vacuum oven temperatures above 60°C were avoided. Since the salts are intrinsically of low hygroscopicity for the reasons given above, the activity of water in the liquid state remains high and 60°C is sufficient to ensure quantitative removal of water. Thus, unlike the cases of some salts of smaller ΔpK_a , the salts of this study could be dried to truly constant weight.

Salt preparation procedures.

GdmFormate, GdmMS, Gdmtrifluoroacetate, GdmLactate, GdmTf, Gdm bistrifluoromethanesulfonimide, $[\text{CF}_3\text{SO}_2]_2$, TFSI, GdmH₂PO₄ and GdmHSO₄ were prepared by slow addition of calculated masses of Gdm₂CO₃ to a flask containing a known amount of the corresponding anhydrous acid. The reaction flask was cooled by an ice-water bath. If the reaction product remained solid, then it was heated until molten, and then stirred vigorously for ~30 min. to ensure reaction completion and solution homogeneity. The product was dried to constant weight in a vacuum oven at 60 °C.

For GdmTFSI and GdmBF₄, HTFSI and HBF₄ the acids were only available as aqueous solutions. Again the guanidinium cation was added slowly, as the carbonate Gdm₂CO₃, to a icebath-cooled flask containing a calculated amount of the HTFSI or the HBF₄ solution, and stirred vigorously for ~30 min. to ensure homogeneity. The product was vacuum-dried to constant weight (48 hr at 60 °C).

To obtain GdmDCA, GdmCl was first dissolved in methanol, then AgDCA (in small excess) added to the solution with vigorous stirring at 40 °C. The container was covered with Al foil and set aside for 12 days. Solids were then filtered out and the filtrate dried in a vacuum oven at 40 °C. This yielded a light yellow solid with a sharp melting point (see Figure 1), and chemical analysis suggesting 97% purity. sufficient for the purposes of this survey.

GdmNO₂ was prepared by a metathetical reaction. NaNO₂ and GdmCl (in small excess) were dissolved in methanol and stirred vigorously at room temperature for 2 days. Then a small amount of AgNO₂ was added to remove the excess chloride as AgCl. leaving pure GdmNO₂. Again the melting point was sharp (Figure 1)

GdmFeCl₄ was particularly simple to obtain. Pure anhydrous GdmCl was mixed with FeCl₃ (98%) powder in a glass vial in an argon filled glove box, sealed and removed for external melting to a clear liquid, with melting point of 99K.