ANION EFFECTS ON THE DYNAMICS OF DEEP EUTECTIC SOLVENTS BASED ON TRIS SALTS AND ETHYLENE GLYCOL

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Deep eutectic solvents (DESs) are a class of materials combining properties of fluids and electrolytes which exhibit unique characteristics, such as high dissolving ability, a wide electrochemical window, low volatility, and a high boiling point. Additionally, their constituents (in the case of type III DESs, a hydrogen bond donor and a hydrogen bond acceptor) are often inexpensive and environmentally benign, making DESs an attractive choice for "green chemistry".

Even though the first DESs were discovered over 20 years ago, our knowledge of how the nature of their components influences their properties is still limited. For example, substitution of the anion in the electrolyte component of DESs remains largely unexplored in the literature. This is mainly due to the difficulty or high cost of ion-exchange processes required to replace the anion in choline chloride and tetraalkylammonium salts, which are typical hydrogen bond acceptors in most studied DESs. In contrast, protic ionic substances, formed by proton transfer from a Brønsted acid to a Brønsted base, do not exhibit this drawback.

In the present work, we investigated the influence of the anion on the dynamics of Tris (tris(hydroxymethyl)aminomethane) protic salts in ethylene glycol (EG) using dielectric relaxation spectroscopy. We show that, within the covered frequency range of $0.05 \leq \nu / \mathrm{GHz} \leq 89$, the obtained spectra can be described as a superposition of relaxation processes arising from Tris-associated species and EG dipoles. For the latter, processes exhibiting nearly unperturbed dynamics were found, as well as contributions considerably slowed down by the solute. The extracted effective solvation numbers of the Tris salts strongly correlate with the strength of anion–solvent interactions, decreasing in the order chloride > nitrate > perchlorate. A Tris cation slows down the dynamics of ~16 EG molecules at infinite dilution. One of them is essentially "frozen" and rotates together with the cation as a single entity. Analysis of the effective dipole moments indicates that, up to concentrations of about 1.5 M, the solutions are dominated by contact ion pairs, before gradually transitioning to the behavior of a "solvent-lubricated" molten salt.

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