

Prototropism and Aggregation within Deep Eutectic Solvents

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Abstract

DESs have been rapidly growing and are becoming solubilizing media of prominence in different aspects of science and technology. They have turned out as notable alternatives for conventional organic solvents and ionic liquids in diverse fields. Therefore, the objectives of the thesis work are designed to advance the understanding of these nascent DESs and help in assessing their untapped potential. The thesis initially explores the sustainability of DESs as a potential solubilizing media for prototropism. The strategy entails a spectroscopic investigation of the prototropic behavior of various fluorophores within judiciously selected DESs. A series of prototropes is investigated to comprehend the role of the structure and functional groups of the probe and also the solubilizing media. Specifically, the prototropic forms of three structurally-distinct hydroxy naphthoic acid derivatives were investigated within two DESs, constituted of H-bond acceptor Choline chloride (ChCl) and different H-bond donors (HBDs), urea and glycerol (Gly), respectively, in 1:2 mole ratio. The study revealed that in contrast to common polar solvents where both monoanionic and neutral forms of 1,2-HNA are present, only the neutral form was observed within both DESs. However, 3,2-HNA exhibits the presence of both anionic and neutral prototropic forms within ChCl:Gly DES, while only the monoanionic form is observed within ChCl:Urea. Even the addition of high strength of acid to ChCl:Urea does result in the formation of a neutral emitting form. As expected, 6,2-HNA exists in its neutral emitting form in ChCl:Urea and in anionic(carboxylate) form in ChCl:Gly owing to the difference in their H-bond donor acidity. It was observed that the addition of acid leads to the formation of a neutral form in ChCl:Urea while no significant changes were observed in ChCl:Gly. The dianionic form is the dominating emitting form in both DESs in the presence

of minimal amount of base. It is inferred that DES constituents and the structure of the probe play a complex interplay in controlling the prototropic equilibria.

Subsequently, the prototropic behaviour of 1-naphthol, 2-naphthol, 1-naphthylamine and 1,8-bis(dimethylamino)naphthalene (DMAN) was examined in type-III ChCl-based DESs prepared by mixing urea, tetraethylene glycol (TEG), 1,4-butanediol (BD), ethylene glycol (EG), and Gly as HBDs with ChCl. Among the investigated probes, 2-naphthol, 1-naphthol, and 1-naphthylamine behave as strong photoacids, whereas DMAN is a powerful photobase. For 2-naphthol, the neutral form is the only absorbing and emitting form observed in all the investigated DESs indicating absence of excited-state proton transfer (ESPT) in these DESs. 1-Naphthol is predominantly present in its neutral form in the ground-state within all the DESs. However, both neutral and anionic forms of 1-naphthol are supported in the excited-state of ChCl:Urea, whereas the neutral form remains the preferred form in other DESs. Similar to 2-naphthol, the 1-naphthylamine also exhibits only neutral form in ground- and excited-state suggesting the lack of ESPT in the DESs. The cationic form of DMAN remains the dominant prototropic form in ground- and excited-state in all the investigated DESs upholding the high photo-basicity of this probe in DESs as well.

The thesis also features the preparation of neoteric lanthanide metal salt-based DESs and a detailed characterization of their physical properties. The type IV DESs prepared in the study are composed of lanthanum nitrate hexahydrate (La), cerium nitrate hexahydrate (Ce), and gadolinium nitrate hexahydrate (Gd) with urea in varying concentrations. The glass transition temperature (T_g) values of all the investigated mixtures were well below room temperature indicating strong interactions between the molecular and ionic components within the eutectic mixture. For effective utilization of these neoteric media, assessment of their physical properties is essential. Thus, the density and dynamic viscosity of different possible eutectic mixtures of La:Urea, Ce:Urea and Gd :Urea are reported in the temperature range

293.15 to 363.15 K. Overall, both density and dynamic viscosity were found to decrease with increasing urea concentration. The density of DESs showed a linear decrease with increasing temperature while temperature dependence of the dynamic viscosity followed Vogel–Fulcher–Tammann (VFT) expression.

The thesis next presents intermolecular aggregation of a widely recognized PAH pyrene followed by a detailed study of self-assembly behaviour of common ionic and non-ionic surfactants within lanthanide salt based-DESs. The pyrene self-aggregation is not known to occur at μM concentration in isotropic solvents and common liquids including organic solvents, ionic liquids, or other DESs. However, La:Urea and Gd:Urea DESs of varying compositions support aggregation of pyrene at unprecedented low concentrations manifested by a broad structureless band along with the signature high energy vibronically-resolved structured emission. Next, the aggregation behaviour of anionic surfactant SDS, cationic surfactant CTAB, and non-ionic surfactant TX-100 is studied within Ce:Urea and La:Urea. The micelle formation is established by using the fluorescence probe PyCHO which showed a change in fluorescence intensity with varying surfactant concentration. Three different eutectic mixtures of La:Urea are explored to understand the role of urea on the aggregation behaviour of both ionic and non-ionic surfactants. In addition to DES composition, effect of temperature on micellization is also investigated for all three surfactants. The high cohesiveness and hydrophilic nature of these DESs brand them as suitable candidates to support micellization process. In brief, it is suggested that DESs may prove to be an efficient solubilizing media for both prototropism and aggregation with potential applications in both academia and industries.