

Spectroscopic Investigation to Reveal Physicochemical Properties and Aggregation Behavior of Deep Eutectic Solvent Derived Systems

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Abstract

The noteworthy potential of deep eutectic solvents (DESs) as environmentally-benign solubilizing media is well-known. Their distinctive and fascinating characteristics coupled with their numerable applications in various industries and academia make them solvents of utmost importance. In this context, the present thesis provides an in-depth description of DESs along with their application to study specific research problems for further widening the scope of this alternate media. The thesis features the investigation of lithium chloride-added (Choline Chloride + Urea) DES as a suitable electrolyte for lithium-ion batteries. The strategy entails a comprehensive investigation of the fluorescence quenching of pyrene (Py) by well-known quencher nitromethane within the system along with the bulk property measurements like density and dynamic viscosity. Excited-state intensity decay of Py shows that the addition of LiCl results in a slight decrease in the decay time because of the presence of chloride ions (Cl^-), which facilitates nonradiative decay pathways of excited Py. The Py-nitromethane fluorophore-quencher pair follows simplistic Stern-Volmer formulation suggesting the quenching to be purely dynamic in nature affording dynamic quenching constant (K_D) and bimolecular quenching rate constant (k_q) in the process. The k_q first increases as LiCl is added to DES ChCl:Urea before decreasing monotonically on further addition of LiCl. This is attributed to the effective role of the microscopic structure of LiCl-added ChCl:Urea over dynamic viscosity in controlling molecular diffusion and dynamics is amply highlighted.

The thesis also explores the physicochemical properties of newly emerged hydrophobic DES TBAC:DA (tetra-*n*-butylammonium chloride + *n*-decanoic acid in 1 : 2 mol ratio) which

will help in tapping the hidden potential of this class of DESs. A detailed investigation of Py fluorescence and its quenching by five different aromatic and aliphatic nitro compounds, such as nitromethane, nitrobenzene, 4-nitrobenzaldehyde, 1-chloro-4-nitrobenzene, and 4-nitroanisole, within TBAC:DA is carried out to investigate the polarity and solute dynamics offered by the DES. This information also highlights the potential of this DES in the detection of explosive nitro compounds. As expected, Py I_1/I_3 ratio suggests the dipolarity of TBAC:DA to be much lower than several common hydrophilic DESs and ionic liquids. Furthermore, the Py fluorescence is quenched effectively by all five quenchers within TBAC:DA; the quenching is most prominent for nitrobenzene. It is inferred that the quenching within this hydrophobic DES is a complex interplay of the reduction potential of the quencher and the presence of the substituents on the quencher imparting steric hindrance to the fluorophore–quencher approach.

Next, this work provides the information regarding the charge-transfer complex formed between acceptor Py and donor *N,N*-dimethylaniline (DMA) in DES TBAC:DA. Charge-transfer fluorescent complex formation between Py and DMA is not supported either in high-viscous ChCl-based DESs or in low-viscous IL, however, TBAC:DA with intermediate dynamic viscosity does support the formation of fluorescent Py-DMA charge-transfer complex. This observation places the non-polar nature of this DES in perspective. The Py-DMA complex formation within TBAC:DA takes place at sub-nanosecond regime, and is facilitated by the presence of weak ground-state interaction between Py and DMA. Also, the Py-DMA complex formation efficiency increases with an increase in temperature and reaches maxima at 298.15 K before decreasing with a further increase in temperature. The initial reduction in dynamic viscosity favors Py-DMA complex formation; this effect is overcome by preferential thermal deactivation of Py-DMA fluorescent complex as compared to the thermal deactivation of Py.

The thesis also features the formation and characterization of water-in-oil microemulsions using the hydrophobic DES TBAC:DA as the oil phase and non-ionic surfactant TX-100 as an emulsifier. The water pools are formed within TBAC:DA under ambient conditions with maximum water loading ($w_0 = [\text{water}]/[\text{TX-100}]$) of 60 ± 3 for $[\text{TX-100}] = 0.3 \text{ M}$. The formation of the microemulsions is established using fluorescence probe pyranine, uv-vis absorbance of Co^{II} , and electrical conductivity measurement. The characterization of these microemulsions is also carried out using the DLS technique which reveals that the average aggregate sizes are in the range of $72(\pm 4)$ to $122(\pm 7)$ nm. These novel water-in-DES microemulsions are then explored as potential solvent systems for solubilizing curcumin with an eye towards establishing its biomedical applications. Under the optimized conditions, excellent uptake of curcumin was observed in this system as compared to that in water, a choline-based IL, and other DESs. The water-in-TBAC:DA microemulsion formed using 0.3 M TX-100 dissolves $\sim 51 \text{ mg/mL}$ of curcumin without compromising its structural integrity. This microemulsion system also exhibited improved stability of curcumin towards sunlight and shelf storage. The overall outcomes of this work successfully provide a groundwork for the utilization of these environmentally-benign DESs in sustainable research and development benefiting science and technology as well as humankind.