Radiation chemical studies of Ionic Liquids & Deep Eutectic Solvents

▪ Synthesis of IV-VI Semiconductor Nanomaterials

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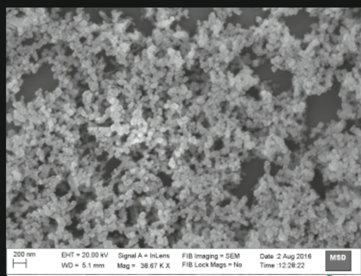
The Deep Eutectic Solvents (DESs) and Room Temperature Ionic Liquids (RTILs) are amongst the emerging exotic solvents being considered as potential alternatives to the conventional hazardous volatile organic solvents (VOCs).

In true spirit of *"energy and environment sustainability"* the aim of this thesis has been to explore how much and to what extent these solvents can act as a potential replacement of VOCs for utility in the back end cycle of nuclear energy program (reprocessing and waste management) as well as in other energy related applications wherein these solvents are susceptible to strong oxidizing or reducing conditions. DESs and RTILs can be better suited for such applications only under the condition that their radiation stability is understood properly. However, high cost of production and purification limits overall acceptance and applications of RTILs to a certain extent, which led to the emergence of DESs, which are relatively cost-effective, non-toxic, biodegradable with facile waste-free synthesis procedure requiring no post-synthetic purification in contrast to the RTILs.

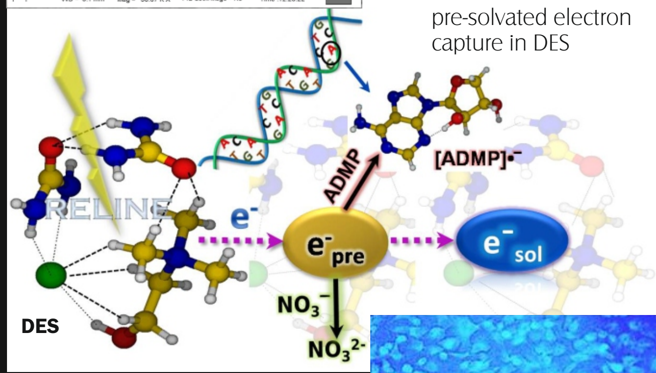
Some of the primary questions that the thesis addresses convincingly are; what are the transient species that would be generated within these two new solvents upon exposure to ionizing radiation? How and to what extent these transient species would affect the performance of these solvents? Is it possible to predict a radiation and chemically stable DES by computational methods for use in radiation related applications? How effectively these solvents can be used as host matrix and stabilizing medium for the synthesis of nanomaterials by radiation assisted technology?

The doctoral thesis has identified and characterized the new transient species; dicyanamide dimer radical anion $(DCA)_2^{\bullet-}$ within ionic liquid $Pyrr_{13}$ DCA; which remains stable in the medium for hundreds of microseconds and is strongly oxidizing in nature. The results obtained in this particular work conclusively indicate that the case of $Pyrr_{13}$ DCA is unique; as in this medium both the solvated electrons (strongly reducing) and the long-lived oxidizing species $(DCA)_2^{\bullet-}$ are produced simultaneously and both can mediate the radiation chemistry in this medium, which warrants special attention in its energy related applications. The primary reducing species, i.e. the pre-solvated electron was observed for the first time in DESs in nanosecond timescale; and could be efficiently captured using DNA base adenosine. These results are important considering the research related to reductive DNA damage.

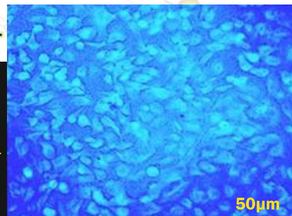
Additionally, a new redox and radiation stable DES composed of 1:2 molar ratio of choline acetate and malonic acid has been comprehended through computational and experimental techniques. Application of a particular solvent in the emerging field of semiconductor nanomaterials synthesis makes it versatile. In this context, both RTIL and DES have been successfully utilized as stabilizing media in nanomaterial synthesis with defined morphology and properties. For nanomaterial synthesis, novelty of radiation chemical method over other contemporary techniques has been highlighted. Photo luminescent tin oxide nanoparticles could be synthesized via radiation chemical technique in the DES reline,



FESEM images of mesoporous SnSe nanoparticles synthesized via e-beam irradiation in $[EMIM][EtSO_4]$



Electron solvation and pre-solvated electron capture in DES



Human lung epithelial carcinoma (A549) cells treated with photoluminescent SnO_2 NPs showed bright blue fluorescence upon excitation using UV filter

which were found to be non-toxic with suitable application in cell imaging. Further, in the RTIL $[EMIM][EtSO_4]$, mesoporous SnSe with high porosity could be synthesized via electron beam irradiation, shows potential applications in sensing, catalysis and photovoltaics.

(The Ph.D. dissertation was supervised by Dr. Soumyakanti Adhikari, Head, Scientific Information Resource Division, BARC)

Dr. Laboni Das, Scientific Officer/E in Radiation and Photochemistry Division of BARC, works in the field of Radiation Chemistry and Nanomaterials. Her research interests include radiation chemical studies of exotic solvents (e.g. deep eutectic solvents, room temperature ionic liquids) and their application in radiation assisted synthesis of semiconductor nanomaterials. She has 10 publications in peer reviewed reputed international journals and 15 conference papers. Dr. Das is a recipient of Homi Bhabha Gold medal from OCES 56th batch (Chemistry discipline).