

CO₂ CAPTURE AND PROTOTROPISM WITHIN ALTERNATE SOLVENT MEDIA

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ABSTRACT

The significant potential of alternate solvents including DESs, ILs, and liquid polymers/surfactants as environmentally-benign solubilizing media and their peculiar and beguiling features coupled to their wide range of applications in various industries and academia make them solvents of utmost importance. In this context, the work presented in the thesis provides a detailed description of these solvents along with their application in studying specific research problems to widen the scope of these alternate solvent. The thesis features an intensive analysis of popular liquid surfactants and polymers for their CO₂ absorption and retention abilities under ambient conditions. Specifically, three Tween (Tween 20, Tween 40, and Tween 80), TX-100, TX-114, and one Pluronic (P84) series liquid surfactants, and three PEG (PEG 200, PEG 400, and PEG 600), and two PEI (PEI 800 and PEI 25000) family liquid polymers are found to capture an appreciable amount of CO₂ in the presence of superbase. Except for PEGs, the efficiency of CO₂ capture is directly correlated to the number of moles of hydroxyl/amine groups present; inter-PEG H-bonding in PEG200 having relatively smaller polymer chain results in partial unavailability of hydroxyl groups to interact with added CO₂. The presence of water within the liquid surfactant/polymer renders the CO₂ uptake by the media faster due to decreased viscosity, the efficiency of CO₂ capture is decreased due to favorable back reaction and H-bonding between added water and hydroxyl of surfactant/polymer. The superbase-added liquid surfactants/polymers exhibit excellent CO₂ capture-expulsion reversibility with alternate CO₂-N₂ addition as well. Further, this thesis includes the preparation of new choline chloride-based eutectic mixtures and a detailed study of their ability to capture CO₂ in the absence and presence of different superbases. The addition of superbase is found to significantly increase the CO₂ capture ability of the DESs as found in the case of liquid polymer and surfactants. Moreover, it is proposed that the reaction of electron-rich centers of hydroxyl/amine functionality present in these solvents (liquid surfactant/polymer and DESs) with the electron-deficient center of CO₂ is facilitated by the superbase. DBN superbase is found to afford more effective capture of CO₂ as compared to DBU and TBD within these alternates solvent media. ¹³C-NMR, FTIR and Raman spectroscopic measurements reveal that a major part of the CO₂ binds covalently to the electron-rich functionalities present on the components of the DES with superbase assisting this association. The reversibility of the captured CO₂ is assessed by introducing N₂ gas into

the CO₂ captured superbase-added DES system and by heating at high temperatures. Intramolecular excimer intensity of BPD and steady-state fluorescence anisotropy of R6G fluorescence probes effectively monitor the CO₂ capture process as the viscosity of the superbase-added DES increases as more-and-more CO₂ is captured.

The work mentioned in the thesis also features a detailed investigation of prototropism within judiciously selected DESs and ILs. A range of DESs and ILs having different structures are used to explore and comprehend the nature of interactions between a prototropic probe and these solvent media. For this purpose, norharmane belongs to β -carboline alkaloid family is selected as a model prototropic probe. In this direction, eight different DESs prepared using ChCl with eight different H-bond donors (HBDs) are selected to ascertain their role in controlling prototropism. In the ground-state, DESs with HBDs glycerol and ethylene glycol support both neutral and cationic forms of norharmane, however, within DESs constituted of HBDs urea, 1,4-butane-diol, and acetamide, respectively, only the neutral form exists. Within the remaining three DESs with HBDs tetraethylene glycol, 3-phenylpropionic acid, and malonic acid, respectively, only cationic form is supported. As the cationic form is preferred more over the neutral form of norharmane in the excited-state, DESs with HBDs tetraethylene glycol, 3-phenylpropionic acid, and malonic acid, respectively, support only the cationic form in the excited-state. DES with glycerol also supports only the cationic form in the excited-state, DES with ethylene glycol, acetamide, and 1,4-butane-diol support both cationic and neutral forms. A good correlation between the common empirical solvent polarity parameter, E_T^N , along with Kamlet-Taft parameters, H-bond donating acidity (α), and H-bond accepting basicity (β), of the DESs and the relative presence of the norharmane prototropic forms is established. Similarly, nine ILs are judiciously selected on the basis of the availability of acidic proton in the cationic part of IL to assess their role in prototropic behavior of norharmane. Experimental outcomes have shown the dependence of norharmane prototropic species on the structural constituent of both cation and anion of the ILs. The role of the acidity imparted via the cation of an IL plays a crucial role in deciding the prototropic behavior of the probe norharmane in ILs. Further, for ILs having similar acidity cations, the Lewis basicity (viz., water-miscibility) of the anionic counterpart of the IL controls the relative presence of the different prototropic forms. ILs as designer solvents to control the prototropic forms of a solute is clearly established. To conclude, the overall outcomes of this work would be helpful to establish DESs, ILs, and liquid polymers/surfactants as environmentally-benign solubilizing media with potential applications in both academia and industry.