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# Fluorescence quenching of polycyclic aromatic hydrocarbons within deep eutectic solvents and their aqueous mixtures



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#### ARTICLE INFO

#### ABSTRACT

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Two common and popular deep eutectic solvents (DESs) composed of the salt choline chloride and H-bond donors glycerol and urea in 1:2 mol ratio named glyceline and reline, respectively, are investigated for the analysis of polycyclic aromatic hydrocarbons (PAHs) using quenching of both steadystate and time-resolved fluorescence of ten different PAHs by nitromethane at 30 °C. Based on their quenching efficiencies, the PAHs are divided into two groups - group 1 is constituted of the five PAHs whose fluorescence are quenched less effectively by nitromethane whereas the other five exhibiting high quenching efficiency are associated to group 2. Quenching of steady-state fluorescence of group 1 PAHs by nitromethane, albeit not very significant, follow a simple Stern-Volmer behavior. The excited-state emission intensity decay of these PAHs, in both absence and presence of nitromethane, fit best to a single exponential model with small but monotonic decrease in lifetimes. The decrease in lifetime also follows Stern-Volmer behavior, however, the quenching constants  $(K_{\rm D})$  are lower than those obtained from steady-state fluorescence ( $K_{SV}$ ). This is ascribed to the possible formation of charge-transfer complex between the PAH and the nitromethane. Steady-state fluorescence quenching of group 2 PAHs exhibit distinct upward curvature from linear Stern-Volmer behavior implying highly efficient quenching. The intensity decay fits best to a double exponential decay model with longer of the decay times following simple Stern-Volmer behavior. Formation of a complex or the presence of nitromethane within the quenching sphere of action of the PAH having short decay time is proposed. Quenching behavior was found to be similar irrespective of the identity of the DES. A representative group 2 PAH, pyrene, is employed to investigate diffusion dynamics within aqueous mixtures of the two DESs. The bimolecular quenching rate constant  $(k_q)$  is found to increase linearly with the mole fraction of water  $(x_w)$  in aqueous mixtures of both the DESs. Stokes-Einstein relationship is not obeyed within the DES aqueous mixtures and is attributed to be due to the inherent heterogeneity of the mixtures. Diffusion dynamics of pyrenenitromethane pair is compared with that of a tracer fluorescein isothiocyanate obtained using fluorescence correlation spectroscopy. Good correlation between the two highlights generality of diffusion dynamics with aqueous DES mixtures as far as solutes are concerned.

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#### 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a major class of environmental pollutants. Many of the common and ubiquitous PAHs are classified as chemical carcinogens and mutagens [1–3]. They have long been classified as priority pollutants by US Environmental Protection Agency (EPA) and are becoming an increasing concern due to their significant human exposure [4]. Due to their resistance to biodegradation they are very persistent in the environment [1,2,5]. The presence of these persisted PAHs in environment may lead to plethora of problems which includes

\* Corresponding author. E-mail address: sipandey@chemistry.iitd.ac.in (S. Pandey). cancer and genetic mutation [5,6]. The detrimental properties of PAHs coupled to growing awareness of environmental pollution prompted researchers to develop analytical methods to isolate the individual organic compounds of this class. In order to detect, identify, and separate PAHs, fluorescence spectroscopy offers high sensitivity and selectivity because the fluorescence quantum yield of most PAHs is quite significant [7–16]. Subsequently, a common way to identify, separate, and categorize PAHs is by utilizing the extent and efficiency of the quenching of the fluorescence emission from the PAHs by suitable quenchers, such as, acrylamide, amines, carbon disulfide, heavy metal ions, chlorinated compounds, halogens, nitromethane and other nitro compounds, nitroxides, nitric oxide, oxygen, picolinium nicotinamide, among others [17]. In this context, nitromethane has been used extensively as a quencher for the fluorescence of PAHs [7–13].

Deep eutectic solvents (DESs) have emerged as low-cost, nottoxic, biodegradable alternatives to not only the traditional organic solvents but also to the room temperature ionic liquids [18,19]. They are promising candidates for a broad range of applications including chemistry, engineering, nanoscience, and biomass processing [20-24]. In contrast to traditional ionic liquids, which exclusively contain ions, the constituents of a DES include a molecular hydrogen bond donor species, in addition to ions. Development of an H-bonding network within a DES is essential for eutectic formation and can be expected to profoundly influence the structural and dynamical aspects of a DES. As many of the inexpensive, common, and popular DESs are hydrophilic in nature, it is convenient to formulate aqueous hybrid milieu constituting of DES and water having vastly varying physicochemical properties that depend on the composition of the mixture [25-28]. Establishing DESs and their aqueous mixtures for PAH analysis utilizing

nitromethane fluorescence quenching affords understanding of the microscopic diffusion dynamics, which ultimately defines the macroscopic transport properties of DESs and their aqueous mixtures. We present the results of our investigation of fluorescence quenching of ten different PAHs (structures provided in Fig. 1) by nitromethane within two common and popular DESs constituted of the salt choline chloride mixed with H-bond donors glycerol and urea, respectively, in 1: 2 M ratio named glyceline and reline (Fig. 2) at 30 °C using both steady-state and time-resolved techniques. Pyrene fluorescence quenching by nitromethane is employed to investigate diffusion dynamics within aqueous mixtures of glyceline and reline, respectively. Results from fluorescence correlation spectroscopy (FCS) are used to support and generalize the outcomes of the diffusion dynamics within aqueous DES mixtures.



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