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Effective Recognition of Lithium Salt in (Choline Chloride: Glycerol) Deep Eutectic Solvent by Reichardt's Betaine Dye 33

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Abstract: Deep eutectic solvents (DESs) have emerged as novel alternatives to common solvents and VOCs. Their employment as electrolytes in battery has been an area of intense research. In this context, understanding changes in physicochemical properties of DESs in the presence of Li salts becomes of utmost importance. Solvatochromic probes have potential to gauze such changes. It is reported herein that one such uv-vis molecular absorbance probe, Reichardt's betaine dye 33, effectively manifests changes taking place in a DES Glyceline, composed of H-bond accepting salt choline chloride and H-bond donor glycerol in 1 : 2 molar ratio, as salt LiCl is added. Lowest energy intramolecular charge-transfer absorbance band of this dye exhibits 17 nm hypsochromic shift as up to 3.0 molal LiCl is added to Glyceline. The estimated E_T^N parameter shows linear increase with LiCl mole fraction. Spectroscopic responses of betaine dye 33, *N,N*-diethyl-4-nitroaniline and 4-nitroaniline are used to assess empirical Kamlet-Taft parameters of dipolarity/polarizability (π^*), H-bond donating acidity (α) and H-bond accepting basicity (β) as a function of LiCl concentration in Glyceline. LiCl addition to Glyceline results in increase in α and no change in π^* and β. It is proposed that added lithium interacts with oxygen of the –OH functionalities on the glycerol rendering the solvent with increased H-bond donating acidity. It is observed that pyrene, a popular fluorescence probe of solvent polarity, does respond to the addition of LiCl to Glyceline, however, the change in pyrene response starts to become noticeable only at higher LiCl concentration ($m_{LiCl} \geq 1.5$ m). Reichardt's betaine dye is found to be highly sensitive and versatile in gauzing physicochemical properties of DESs in the presence of LiCl.

Keywords: deep eutectic solvent; reichardt's betaine dye 33; glyceline; lithium chloride; pyrene

1. Introduction

Deep eutectic solvents (DESs) have emerged as viable alternatives not only to the toxic organic solvents but also to the ionic liquids [1-7]. While many commonly used organic solvents are hazardous to the immediate environment and belong to the class of volatile organic compounds (VOCs), recent toxicity reports are not favorable as far as common ionic liquids are concerned [7,8]. Escalating cost associated with the manufacturing of many organic solvents combined with the complexity of synthesis and purification of most ionic liquids are further restricting the use of these solvent media in science and technology today [7,8]. A DES, in this context, affords solubilizing media that is mostly non-toxic and inexpensive. DESs can be prepared by simple mixing of two judiciously selected constituents, one usually H-bond donor (HBD) and the other H-bond acceptor (HBA), that are inexpensive, non-toxic, and easily acquired. After mixing the two constituents, the melting point of the resulting mixture is usually much lower than the melting points of each of the constituents that results in liquid state of matter under ambient conditions. Among several classes of DESs proposed in recent literature, the ones prepared by mixing a common ammonium salt as HBA with a suitable HBD, are perhaps the most investigated so far [3,5,9]. Specifically, the DESs constituted of choline chloride as the HBA and one of the HBDs, namely urea, glycerol, ethylene glycol, and malonic acid, are the initial DESs in this class that were reported around two decades ago [3,5,9]. Applications of these DESs in various strata of science and technology have been growing ever since [2,3].

One of the major areas of applications of the DESs have been in electrochemistry, where DESs have shown potential as worthy electrolytes for batteries [10,11]. As a consequence, salt-added DESs

have become solvent system of rigorous investigations lately. In this context, investigations on potential use of DESs in Li ion batteries have naturally emerged. The changes in the physicochemical properties of the DESs due to the presence of Li salt have subsequently become an active area of research. Understanding of solvation and dynamics of Li salts within DESs is being pursued by researchers worldwide.

Solvatochromic probe behavior within Li salt-added DES system can reveal the changes in the physicochemical properties of the milieu due to the addition of the Li salt; it also reveals information on solute solvation and dynamics in the processes [12–14]. Information gained from the responses of spectroscopic probes can be useful in understanding reactivity, separation, extraction, electrochemistry involving the solutes of similar functionalities. We have found that Reichardt's betaine dye 33 (structure provided in Figure 1), which is known to manifest dipolarity/polarizability along with H-bond donating (HBD) acidity of the solubilizing medium, is effectively able to gauze the consequences of adding LiCl to the DES constituted of choline chloride (ChCl) and glycerol (Gly) in 1 : 2 molar ratio named Glyceline. The use of betaine dyes to obtain physicochemical changes and solute solvation affords a simple and effective way to obtain insights to such complex systems.
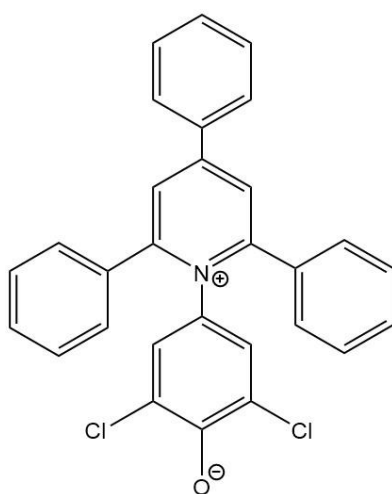

Figure 1. Structure of Reichardt's betaine dye 33.

2. Materials and Methods

Glycerol (≥99.5%), choline chloride (≥99.0%) and LiCl with >99% (by mass) purity were purchased from Sigma-Aldrich and stored in the Auto Secador desiccator cabinet. 2,6-Dichloro-4-(2,4,6-triphenylpyridinium-1-yl)phenolate (betaine dye 33) was purchased in the highest available purity from Fluka (≥99%, HPLC grade). 4-Nitroaniline (NA) and *N,N*-diethyl-4-nitroaniline (DENA) were purchased in the highest purity from Spectrochem Co. Ltd. and Frinton Laboratories, respectively. Pyrene [≥99.0% (GC), puriss for fluorescence] was obtained in highest purity from Sigma-Aldrich Co.

The calculated amount of glycerol and choline chloride was transferred to a glass vial and weighed using an analytical balance with a precision of ±0.1 mg. The components were mixed thoroughly to obtain a homogeneous solution and subjected to vacuum for approximately 6 hours. As per the requirement, pre-calculated amount of LiCl was added to this solution and mixed over magnetic stirrer at 60°C until all of the LiCl was dissolved, and a homogeneous solution was obtained. Stock solution of all probes were prepared by dissolving required amount in ethanol in a pre-cleaned amber glass vial and stored at 4±1°C to retard any photochemical reaction. An appropriate amount of the probe solution from the stock was transferred to the 1 cm path length quartz cuvette. Ethanol was evaporated using a gentle stream of high purity nitrogen gas to achieve the desired final concentration of the probe. Pre-calculated amount of LiCl added – Glyceline DES was directly added to the cuvette and the solution was thoroughly mixed. The final concentrations of DENA, NA, betaine

dye 33 and pyrene were ~20, 20, 50 and 10 µM, respectively. A Perkin-Elmer Lambda 35 double beam spectrophotometer with variable bandwidth was used for the acquisition of the UV−Vis molecular absorbance spectra of DENA, NA and betaine dye 33. Steady-state fluorescence spectra of pyrene (λ_{ex} = 337 nm) were acquired on an Edinburgh Instruments Ltd. spectrofluorimeter (FLS1000-SS-S) with STGM325-X grating excitation and STGM325-M grating emission monochromators with a 450 W Xe arc lamp as the excitation source, a single cell TEC holder and a Red PMT as the detector. All spectra were duly corrected by subtracting the spectral responses from suitable blanks prior to data analysis. Data analysis was performed using SigmaPlot v14.5 software.

3. Results and Discussion

UV-Vis molecular absorbance spectra of Reichardt's betaine dye 33 dissolved in LiCl-added Glyceline under ambient conditions are presented in Figure 2A (the maximum molal concentration of LiCl in the system was $\boldsymbol{m_{LiCl}}$ = 3.0 mol.kg^{-1}, which corresponds to mole fraction $\boldsymbol{\chi_{LiCl}}$ = 0.24). A careful examination of the spectra reveals that the lowest energy absorbance band of the dye shows systematic monotonic hypsochromic shift as LiCl is added to Glyceline. It is well-established that 2,6-diphenyl-4-(2,4,6-triphenylpyridinium-1-yl)phenolate (Reichardt's betaine dye 30) exhibits an unusually high solvatochromic band shift; the lowest energy intramolecular charge-transfer absorption band of betaine dye 30 is hypsochromically-shifted by ca. 357 nm in going from relatively nonpolar diphenyl ether ($\boldsymbol{\lambda_{max}}$~ 810 nm) to water ($\boldsymbol{\lambda_{max}}$~ 453 nm) [15–17]. It is established that the negative solvatochromism of betaine dye 30 originates from the differential solvation of its highly polar equilibrium ground-state and the less polar first Franck–Condon excited-state with increasing solvent polarity [15–17]. There is a considerable charge transfer from the phenolate to the pyridinium part of the zwitterionic molecule. Because of its zwitterionic nature the solvatochromic probe behavior of betaine dye 30 is strongly affected by the HBD acidity of the solvent; HB donating solvents stabilize the ground-state more than the excited-state. The empirical scale of solvent 'polarity', $\boldsymbol{E_T(30)}$ for betaine dye 30, is defined as the molar transition energy of the dye traditionally in kcal.mol^{-1} at room temperature and normal pressure according to the expression $\boldsymbol{E_T(30)}$ = 28591.5/$\boldsymbol{\lambda_{max}}$ in nm [15–17]. However, in the present work a derivative of betaine dye 30, 2,6-dichloro-4-(2,4,6-triphenylpyridinium-1-yl)phenolate (betaine dye 33), is used to investigate LiCl-added Glyceline system due to its certain advantages over betaine dye 30. The low solubility of betaine dye 30 in many H-bonded solvent systems renders it unsuitable for our investigations. Betaine dye 33, on the other hand, has no such problems due to inherent structural differences with betaine dye 30. For historical reasons, it has been related to number 33, and the lowest energy absorbance transition of this dye [i.e., $\boldsymbol{E_T(33)}$] is calculated the same way $\boldsymbol{E_T(30)}$ is calculated [17].

Thus, from the absorbance spectra of betaine dye 33 presented in Figure 2A, the corresponding $\boldsymbol{E_T(33)}$ are estimated and converted into $\boldsymbol{E_T^N}$ using Equations (1) and (3):

$$E_T(30) = 0.9953(\pm 0.0287) \times E_T(33) - 8.1132(\pm 1.6546) \tag{1}$$

R = 0.9926, standard error of estimate = 0.8320, n = 20

$\boldsymbol{E_T}(30)$ was obtained from $\boldsymbol{E_T}(33)$ (i.e., Equation (1)) by acquiring lowest energy uv-vis absorbance band for both the dyes in 20 different solvents, and performing linear regression analysis between the two.

$$E_T^N = \frac{\left[E_T(30)_{SOLVENT} - E_T(30)_{TMS}\right]}{\left[E_T(30)_{WATER} - E_T(30)_{TMS}\right]} \tag{2}$$

Here, TMS stands for tetramethylsilane. From $\boldsymbol{E_T}(30)_{WATER}$ = 63.1 kcal.mol^{-1} and $\boldsymbol{E_T}(30)_{TMS}$ = 30.7 kcal.mol^{-1}, we obtain

$$E_T^N = \frac{\left[E_T(30)_{SOLVENT} - 30.7\right]}{32.4} \tag{3}$$

E_T^N is easier to conceive as it is dimensionless and varies between 0 for TMS (extreme non-polar) and 1 for water (extreme polar) [17]. Table 1 lists lowest energy absorbance maxima ($\lambda_{max,33}$) of betaine dye 33 along with the estimated E_T^N for the LiCl-added Glyceline system. A hyposchromic shift of 17 nm is observed in going from no LiCl to 3.0 *m* of LiCl in Glyceline which transforms to an increase in E_T^N from 0.86 to 0.95. It is convenient to note that a plot of E_T^N versus χ_{LiCl} exhibits good linear behavior (R² > 0.98) with a slope of 0.36 (±0.02) (Figure 2B). Thus, it is concluded that as LiCl is added to Glyceline, the dipolarity/polarizabilty and/or HBD acidity of the system increases; and the increase is effectively manifested in the spectral response of the Reichardt's betaine dye 33 in a linear manner with the mole fraction of LiCl.

Table 1. Absorbance maxima for Reichardt's betaine dye 33 ($\lambda_{max,33}$), DENA ($\lambda_{max,DENA}$) and NA ($\lambda_{max,NA}$) and corresponding estimated Kamlet—Taft empirical solvent parameters, at different mole fraction of LiCl (χ_{LiCl}) in Glyceline under ambient conditions. Error in λ_{max} are ≤ ±0.5 nm. Error in E_T^N is ≤ ±0.007 and errors in α, β & π^* are ≤ ±0.005.

m_{LiCl} (mol.kg⁻¹)	χ_{LiCl}	$\lambda_{max,33}$ (nm)	E_T^N	$\lambda_{max,DENA}$ (nm)	π^*	$\lambda_{max,NA}$ (nm)	β	α
0.0	0.00	426	0.86	422	1.21	385	0.43	0.85
0.5	0.05	422	0.89	422	1.21	385	0.43	0.89
1.0	0.10	419	0.90	422	1.21	385	0.43	0.92
1.5	0.14	417	0.91	422	1.21	385	0.43	0.94
2.0	0.18	413	0.93	422	1.21	385	0.43	0.98
2.5	0.21	411	0.94	422	1.21	385	0.43	1.00
3.0	0.24	409	0.95	422	1.21	385	0.43	1.02

Whether the increase in E_T^N upon addition to LiCl to the DES Glyceline is due to the increase in the dipolarity/polarizabilty or the HBD acidity or both is explored by assessing empirical Kamlet-Taft solvatochromic indicators of solvent dipolarity/polarizability (π^*), HBD acidity (α), and HBA basicity (β) [18–21]. The π^* is estimated from the absorption maximum (ν_{DENA}, in kK) of DENA, a non-hydrogen bond donor solute, using [18,19]:

$$\pi^* = 8.649 - 0.314\nu_{DENA} \tag{4}$$

and then α was estimated from $E_T(30)$ and π^* values [18,20].

$$\alpha = [E_T(30) - 14.6(\pi^* - 0.23\delta) - 30.31]/16.5 \tag{5}$$

δ parameter in Equation (5) is a "polarizability correction term" equal to 0.0 for nonchlorinated aliphatic solvents, 0.5 for polychlorinated aliphatics, and 1.0 for aromatic solvents. Finally, β values are determined from the enhanced solvatochromic shift of NA relative to its homomorph DENA, – Δν(DENA–NA)/kK [18,21]:

$$\beta = -0.357\nu_{NA} - 1.176\pi^* + 11.12 \tag{6}$$

Interestingly, the uv-vis absorbance spectra of both DENA and NA, respectively, do not show any statistically meaningful variation upon addition of up to 3.0 *m* LiCl to the DES Glyceline (Figure 3A). Based on Equations (4) and (6), this subsequently reflects in no change in the β and the π^* parameters as LiCl is added to Glyceline (Table 1). The parameter α, which depends on E_T parameter along with π^* (Equation (5)), does increase with increasing concentration of LiCl in Glyceline (Figure 3B).
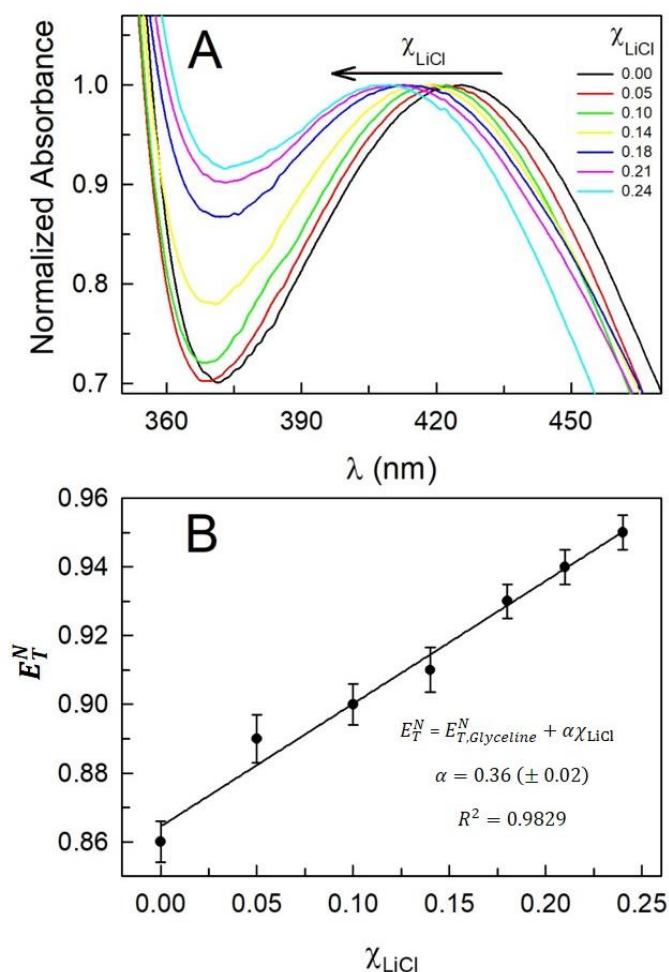
Figure 2. Absorbance spectra of Reichardt's betaine dye 33 [50 µM] in Glyceline and LiCl – added Glyceline under ambient conditions (panel **A**) and variation of E_T^N with mole fraction of LiCl (χ_{LiCl}) (panel **B**). Solid straight line is the best fit obtained from the linear regression analysis. Error in E_T^N is ≤ ±0.007.

The Kamlet-Taft empirical parameters for solvent polarity ($\boldsymbol{\pi^*}$, α, and β) clearly indicate the surprising outcome that as LiCl is added to DES Glyceline, dipolarity/polarizability of the medium does not change, nor does the H-bond accepting basicity – the medium acquires more H-bond donating acidity [parameter α increases linearly with increasing $\boldsymbol{\chi_{\text{LiCl}}}$ within the system with slope = 0.70 (±0.02)]. Within Glyceline, it is reported that the $\textbf{Cl}^-$ of ChCl are involved in H-bonding with the –OH functionalities of glycerol that in turn contributes in DES formation [22]. We believe that added $\textbf{Li}^+$ preferentially combines with oxygen of the –OH functionalities of glycerol thus rendering HBD acidity of the medium to increase. The diminished HBA basicity due to this is compensated by the presence of additional $\textbf{Cl}^-$ of the LiCl. Since both added $\textbf{Li}^+$ and $\textbf{Cl}^-$ are involved in various H-bonding within the system diminishing their charges, no effective increase in dipolarity/polarizability is observed.
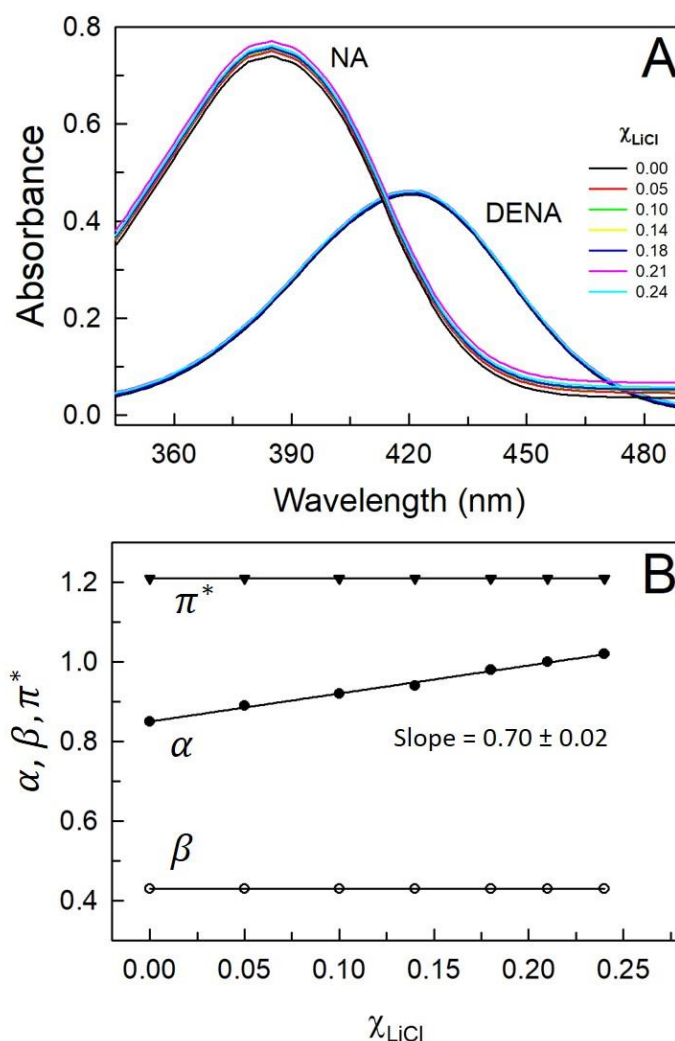
Figure 3. UV-Visible absorbance spectra of N,N-diethyl-4-nitroaniline (DENA, 20 µM) and 4-nitroaniline (NA, 20 µM) (panel **A**) and variation of α, β and π^* with mole fraction of LiCl (χ_{LiCl}) within Glyceline (panel **B**) under ambient conditions. Errors in α, β & π^* are ≤ ±0.005.

Since fluorescence polarity probes are known for their higher sensitivity, we employed pyrene as one of such probes to assess the effect of LiCl addition on DES Glyceline. Fluorescence emission spectra of pyrene is constituted of five vibronic bands with band 1-to-band 3 intensity ratio (Py I_1/I_3) increases monotonically with increasing dipolarity of the pyrene cybotactic region [23-27]. Emission spectra of pyrene in LiCl-added Glyceline is acquired at five different temperatures in the range 298.15 to 358.15 K (representative spectra are shown in Figure 4A).
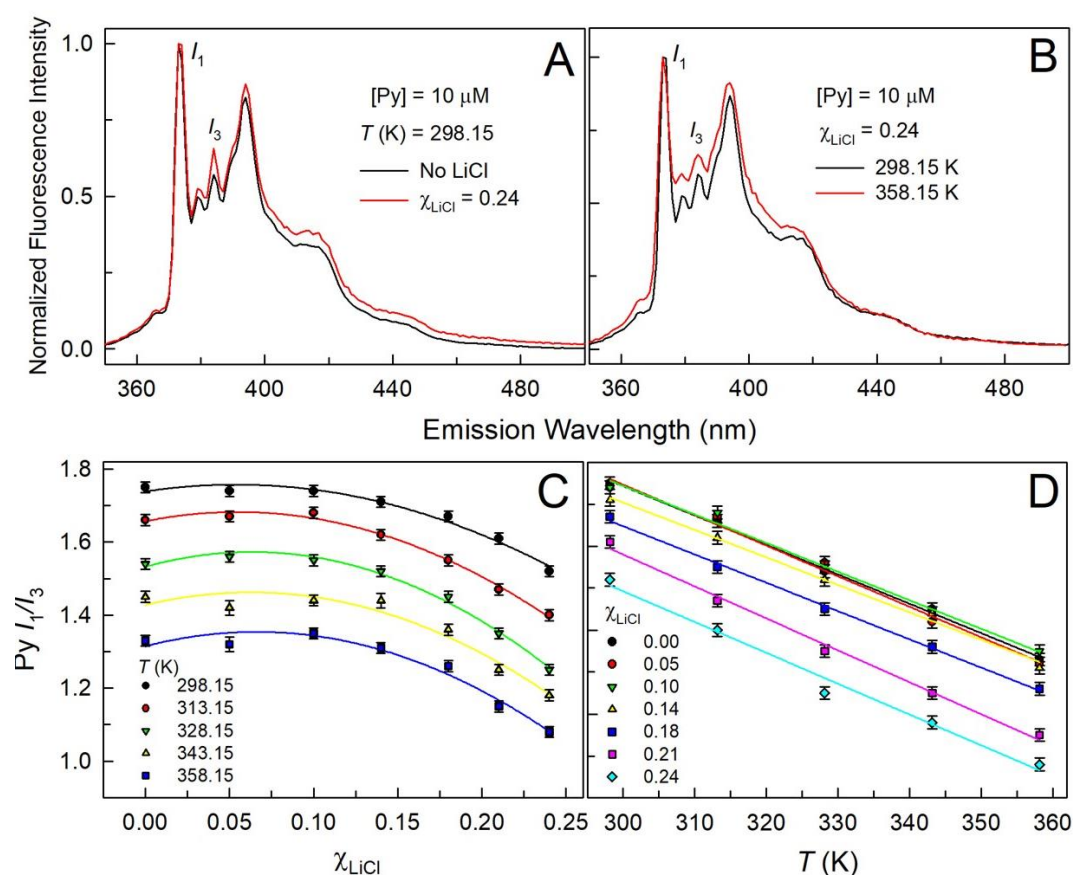
Figure 4. Fluorescence emission spectra of pyrene within Glyceline in the absence and presence of LiCl (χ_{LiCl} = 0.24) at 298.15 K (panel A) and at 298.15 K and 358.15 K at χ_{LiCl} = 0.24 (panel B). Band 1-to 3 emission intensities ratio of pyrene (Py I_1/I_3) within LiCl – added Glyceline for temperatures range between 298.15 to 358.15 K (panel C) and for different LiCl mole fraction at all investigated temperatures (panel D). Error in Py I_1/I_3 is ≤ ±0.02.

The estimated Py I_1/I_3 at different χ_{LiCl} are plotted in Figure 4C. A careful examination of the data reveals that statistically meaningful changes in Py I_1/I_3 start to appear only above 1.5 *m* LiCl – for m_{LiCl} < 1.5 *m*, probe pyrene is not able to manifest polarity changes in the system as LiCl is added to Glyceline; betaine dye 33 response, however, could effectively reflect the changes in the medium at very low LiCl concentrations as well. It is interesting to note that at higher LiCl concentrations, the Py I_1/I_3 decreases suggesting a decrease in the dipolarity of the pyrene cybotactic region in the presence of LiCl. We again evoke the explanation given above that both **Li$^+$** and **Cl$^-$** tie up with the charged species present in the solution thus lowering the dipolarity of the medium – this lowering in dipolarity may be overshadowed by the increased HBD acidity that gets reflected in the response of the betaine dye 33. A further support to this is afforded by the variation in Py I_1/I_3 of the LiCl-added Glyceline as the temperature is increased (Figure 4B shows pyrene emission spectra at two different temperatures). Figure 4D depicts clear decrease in Py I_1/I_3 as the temperature of LiCl-added Glyceline system is increased – the decrease is observed to be linear. This observation is akin with the decrease in static dielectric constants (ε) of several liquids, including several DESs and ionic liquids, as the temperature is increased. Also, similar observations were reported for the LiCl-added ChCl:Urea and glycerol, respectively, as well as LiTf$_2$N-added 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C$_2$C$_1$im][Tf$_2$N]) at similar temperatures [28,29,30].

4. Conclusions

Reichardt's betaine dye 33 is able to effectively manifest the changes taking place in DES Glyceline as salt LiCl is added. Response of the betaine dye 33 in concert with responses from DENA and NA (to obtain empirical Kamlet-Taft parameters) afford a scenario where it is clear that as LiCl is added to Glyceline, the HBD acidity of the medium increases with little or no change in the dipolarity/polarizability and HBA basicity. The interaction of Li species with the oxygens of the –OH functionalities of glycerol imparts increased HBD acidity to the medium with other interactions compensating for each other in such a manner that there is little or no increase in dipolarity/polarizability and HBA basicity. Fluorescence probe pyrene is able to reflect the decrease in the dipolarity but only at higher LiCl concentrations ($m_{LiCl} \geq 1.5\ m$). Decrease in dipolarity with increasing temperature, however, is amply manifested through pyrene response. Sensitivity and versatility of Reichardt's betaine dye in effective gauzing of changes in the physicochemical properties of the liquid medium is amply demonstrated.

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