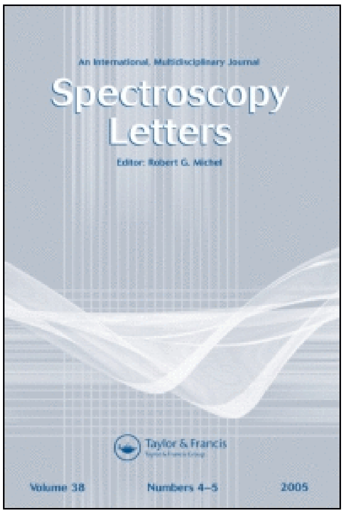

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TOTAL FLUORESCENCE QUANTUM YIELD AND RED SHIFT OF TOTAL FLUORESCENCE MAXIMUM AS PARAMETERS TO INVESTIGATE POLYCYCLIC AROMATIC COMPOUNDS PRESENT IN DIESEL FUEL

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TOTAL FLUORESCENCE QUANTUM YIELD AND RED SHIFT OF TOTAL FLUORESCENCE MAXIMUM AS PARAMETERS TO INVESTIGATE POLYCYCLIC AROMATIC COMPOUNDS PRESENT IN DIESEL FUEL

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ABSTRACT

A method has been developed to find out total fluorescence quantum yield (Φ_F^T) of petroleum products like diesel, which provides the overall fluorescence quantum efficiency of a fluorophore at various possible excitation wavelengths. This simple method is suitable for characterization of petroleum products like diesel. The concentration dependent quantitative investigation of PACs present in diesel with respect to variation in Φ_F^T and red shift of excitation/emission maximum has been studied. The molecular interaction of PACs in fluorophoric mixtures like resonance energy transfer and self-quenching via solvent collision has been explained. Effect of solvent and external quencher molecule on diesel has also

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been studied. Nitrobenzene is found to be a selective quencher for PACs of diesel.

Key Words: Total fluorescence quantum yield; Red shift; TSF; Diesel

INTRODUCTION

Combustion of heavy-duty motor fuels like diesel has been known to be main source of environmental pollution, therefore their rapid regulation in the environment is of interest[1]. Diesel contains host of polycyclic aromatic compounds, which are often carcinogenic and mutagenic. Fluorescence is highly selective for PACs and can be performed directly on diesel. Fluorescence studies of crude oils/petroleum products have provided valuable insight into their fundamental and dynamic properties[2–8]. Recently using 3D fluorescence Smith and Sinski[9] have explained the red shift cascade behavior of synthetic PAH mixture of diesel mimic with concentration.

Most commercial fluorimeters operate with a right angle geometry. In a study of the effect of sample geometry on synchronous fluorescence characteristics of petroleum products we have recently shown that right angle geometry provides greater uniqueness of spectral response to a particular composition of petroleum products in a mixture[3]. The problems associated with the analysis of PACs in multifluorophoric mixture like diesel at higher concentration by a commercial fluorimeter operated at right angle sample geometry are energy transfer, inner filter effects, quenching and self-quenching of fluorophores. Therefore, for specific multifluorophoric sample like diesel at a given excitation wavelength, the fluorescence spectrum and its area/volume will incorporate the effects of the energy transfer, self-absorption, inner filter effect and quenching at higher concentration. Each of these effects is difficult to quantify from a molecular perspective. Despite this, the spectrum and its area/volume can still be taken as a unique representation[2–3,6–7]. Area under a fluorescence spectrum is related to its quantum yield[5–7]. For a multifluorophoric systems, however, the meaning of this quantum yield is different then its usual definition[5]. The dependence of the relative quantum yield on the excitation wavelength could help fluorimetric characterization of various petroleum products/crude oils. Taking this in account Mullins and coworkers[6,7] have done a detailed study on the fluorescence relative quantum yield of crude oils using conventional fluorescence measurement. We have also carried out similar studies for petroleum products using conventional fluorescence, which shows a different behavior compared to crude oils[5].

In this letter we have attempted to define a "relative total fluorescence quantum yield (Φ_F^T)" parameter for multifluorophoric system like diesel using total scanning fluorescence (TSF) technique[8,10,11]. The total fluorescence quantum yield differs from traditional quantum yield measurement that in case of conventional fluorescence measurement the fluorescence efficiency is measured at a particular excitation wavelength, but total fluorescence quantum yield provides the overall fluorescence efficiency of a fluorophore at various possible excitation wavelengths.

EXPERIMENTAL

Sample

Diesel was collected from the local market in the Chennai. To check the spectroscopic validity, test samples from ten different places in Chennai was collected within a time gap of 6 months. Except a minor change in fluorescence intensity no variation in other fluorescence properties was observed for all these samples. Cyclohexane (HPLC grade, Ranbaxy) was used as solvent after purification and was subjected to blank experiments to ensure its fluorimetric purity. Other solvents were spectroscopic grade (SRL), Nitrobenzene (Qualigen). A known volume of pure sample was pipetted out and was made up to the corresponding concentration (in %, v/v) with cyclohexane as desired.

Instrumentation

Fluorescence spectra were obtained on a Hitachi F-4500 spectrofluorimeter. For TSF measurement, the scan speed was 2400 nm/sec and PMT voltage was at 700 V. Excitation and emission slit width were 5 nm. Excitation source was 100 W Xenon lamp. A right angle geometry was used for measurement[3]. For neat samples where the optical densities are high the spectra reflect a combined effect of fluorescence and inner filter effect[3]. The absorption correction was made with respect to pure cyclohexane. For diesel sample fluorescence were collected in the excitation wavelength range 280–550 nm and emission wavelength range 320–650 nm with an interval of 5 nm each.

Relative Total Fluorescence Quantum Yield (Φ_F^T)

In the line of earlier reports[5–7] the relative total fluorescence quantum yield (Φ_F^T) of a petroleum product (diesel) at higher concentration can be defined as

$$\phi_u^T = \left(\frac{P_{PP}(\lambda_{PP})}{P_R(\lambda_R)}\right)\left(\frac{n_{PP}^2}{n_R^2}\right)\left(\frac{(V_{PP} - V_s)_u}{(V_{PP} - V_s)_R}\right) \tag{1}$$

Subscript PP and R refer to the multifluorophoric sample (diesel in our case) of unknown total fluorescence quantum yield and the reference sample respectively. P(λ) is the power reading of power meter including the baseline subtraction and detector response correction at wavelength λ; n_{PP} and n_R are the refractive indices of the unknown petroleum product sample and that of the reference sample respectively; V_{PP} is the total corrected volume under the unknown 3D fluorescence spectrum; V_S is the corrected volume under the unknown 3D fluorescence spectrum over the excitation wavelength bands. Under the conditions of these measurements, larger TSF intensity was obtained for 5%, v/v diesel in cyclohexane and K_F^T of this was taken as unity to calculate relative total fluorescence quantum yields. To find out the volume of the TSF spectrum, a Window based software was employed.

RESULTS AND DISCUSSION

Qualitative Study

The TSF spectrum of neat sample of diesel is given in Fig. 1. The contour map (Fig. 1) gives the distribution pattern of higher member ring PACs present in these systems[8]. As the HOMO-LUMO energy gap decreases with increasing number of rings (increasing conjugations), the S_0-S_1 excitation wavelength increases correspondingly[12,13]. A substitution of the aromatic compounds by alkyl-, phenyl-, or other functional groups shows nearly no influence on the position of the excitation spectra[12,13]. Therefore, compounds having lower number of PAC ring will give a lower excitation/emission maximum and higher number of PAC ring will give a higher excitation/emission maximum. Neat sample of diesel shows two contour points (Fig. 1b) one at around $\lambda_{ex} = 475$ nm & $\lambda_{em} = 600$ nm and the other at around $\lambda_{ex} = 435$ nm & $\lambda_{em} = 470$ nm, which are due to higher member ring (5/6) PACs. Presence of 5- and 6-member ring PACs in diesel is also reported earlier by Mass spectrometer[14,15].

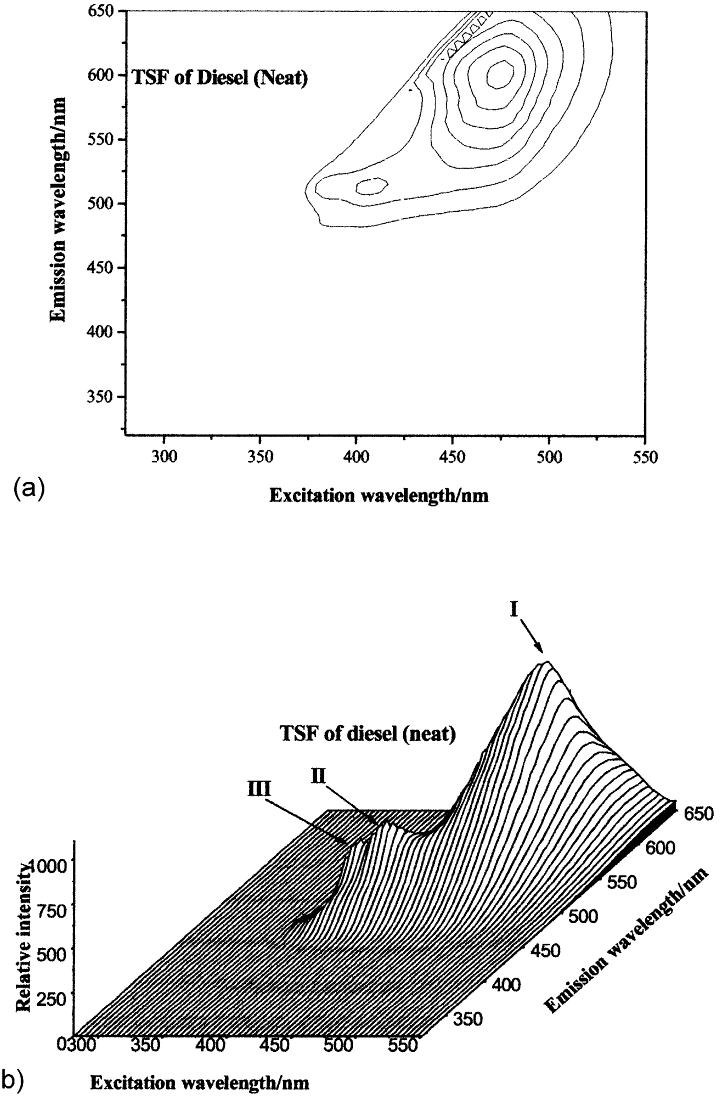

Figure 1. Total scanning fluorescence (TSF) spectrum of neat sample of diesel (scattering uncorrected spectrum) (a) contour map, (b) 3-dimensional diagram. Arrow mark shows the different class of PACs present in diesel.

Quantitative Analysis

The concentration dependent 3D plot of diesel is given in Fig. 2. For diesel, dilution by cyclohexane produces either a blue shift in the excitation and/or emission maximum or generates a new band ($\lambda_{ex}^{max}/\lambda_{em}^{max}$) at lower wavelength range (blue shift band) suppressing the band at the longer wavelength (λ_{SFS}^{max}). In neat diesel, the $\lambda_{ex}^{max}/\lambda_{em}^{max}$ appears at the lower energy range. This is due to extensive resonance transfer[2–7] from lower to higher member ring PACs. With dilution by cyclohexane, the efficiency of relative energy transfer decreases, thereby shifting the $\lambda_{ex}^{max}/\lambda_{em}^{max}$ maxima to blue (Figure 2). It is interesting that the curve in Figure 2 shows discrete jumps (layer blue shift) which is possibly due to the response from different class of PACs present in this system[12]. This blue shift of $\lambda_{ex}^{max}/\lambda_{em}^{max}$ and insensitive

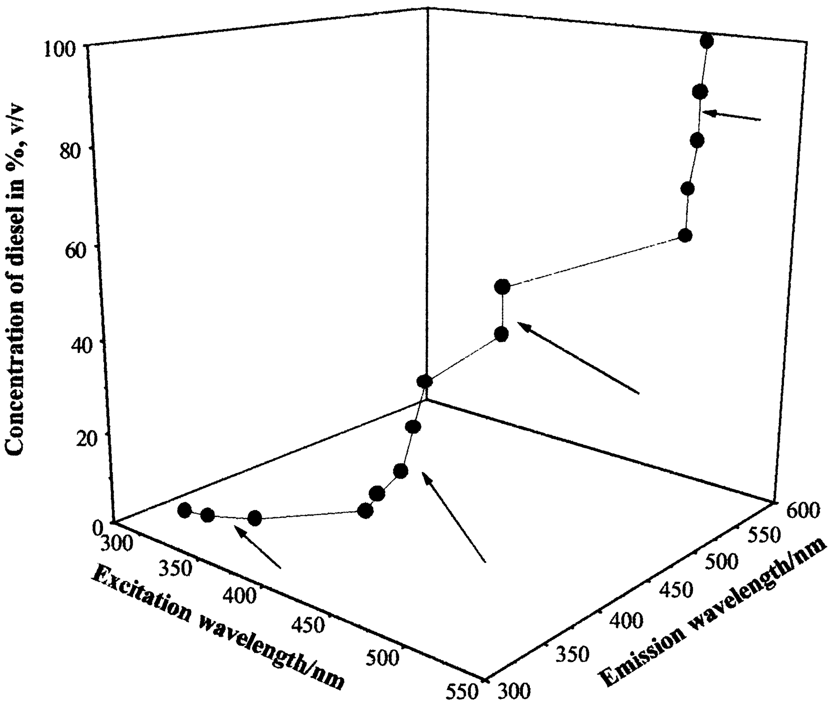

Figure 2. 3-dimensional plot of excitation maximum, emission maximum with diesel concentration. The excitation/emission maxima were obtained from TSF contour map recorded with an interval of 5 nm in excitation/emission scale. Arrow mark shows the different class of PACs present in diesel.

nature of higher $\lambda_{ex}^{max}/\lambda_{em}^{max}$ band of diesel with dilution concludes that the relative concentration of PACs decreases with the aromatic ring size. Recently using Time-of-Flight Mass analysis Hankin and John[15] have also reported that, in general, the relative concentration of polycyclic aromatic compounds decreases from 3- to 6-member ring systems in diesel particulate.

Relative Total Fluorescence Quantum Yield (Φ_F^T)

The relative total fluorescence quantum yield (Φ_F^T) of neat sample of diesel is found out as described as in the experimental section. The Φ_F^T value for neat sample of diesel is 0.78. Fig. 3 depicts the change in Φ_F^T diesel with concentration. Φ_F^T decreases with increasing proportion of diesel and tends to level of at higher concentration ($\sim > 50\%$). An interesting application of such a plot could be its use for estimating adulteration level in diesel. Adulteration of heavy-duty motor fuel like diesel is a serious problem in South Asia[3,16]. Common adulterants like kerosene and industrial solvents

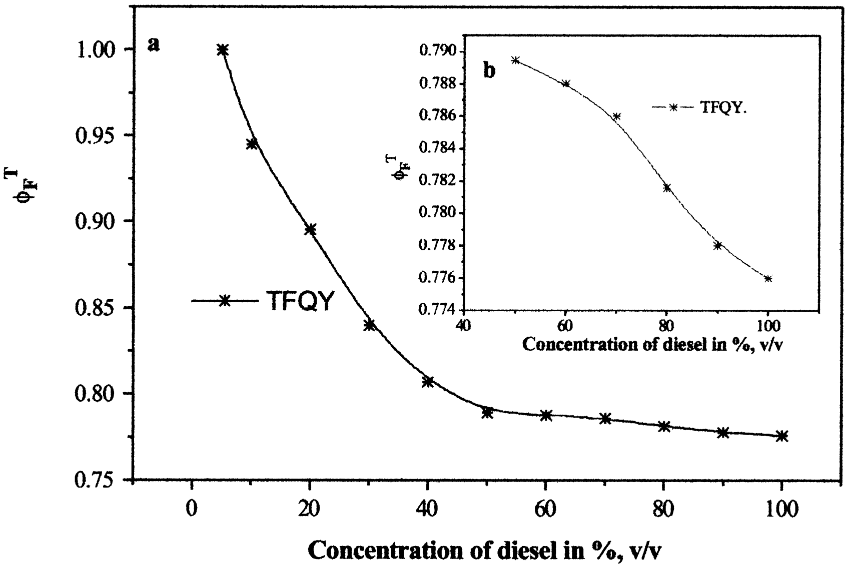

Figure 3. Plot of relative change of total fluorescence quantum yield (ϕ_N^T) of diesel with concentration. The variation of ϕ_N^T with diesel concentration in the range 50–100%, v/v is shown in Fig. b.

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have different PAC contents and their presence is expected to alter Φ_F^T. This possibility needs further investigations.

The change of fluorescence intensity of diesel with concentration at three different excitation/emission maximum points (at band I, II & III of Figure 1b), which is, in fact, response from three different class of polycyclic aromatic compounds, is shown in Fig. 4. This indicates that below 17% v/v of diesel concentration resonance energy transfer between intermediate PACs is the dominant factor, in between 17 to 54%, v/v of diesel concentration resonance energy transfer from intermediate to higher member ring PAC (6 ring system) dominates while above 54%, v/v of diesel concentration self-quenching of larger ring PAC (6 ring system) dominates (as the decrease in fluorescence intensity at $\lambda_{ex} = 475\,\text{nm}$, $\lambda_{em} = 600\,\text{nm}$ cannot be due to resonance energy transfer or inner filter effect). We have

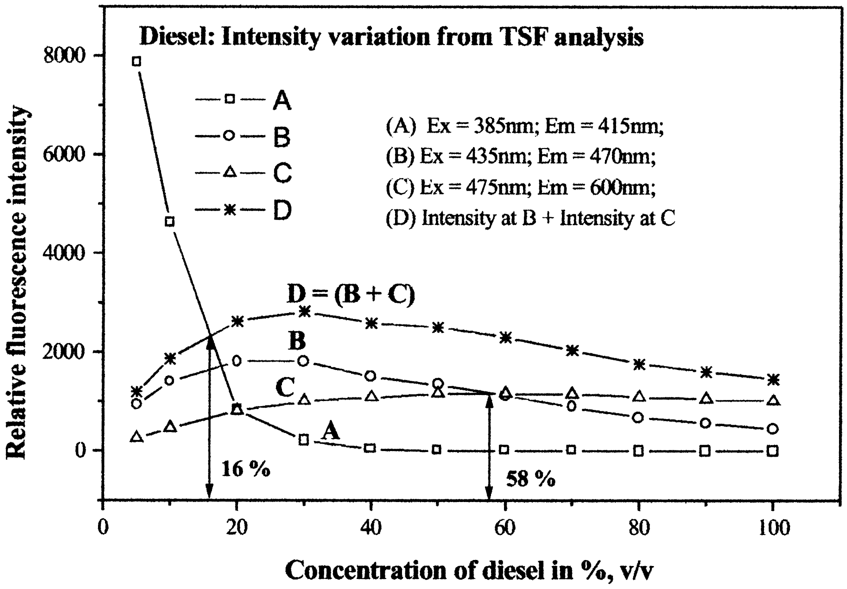

Figure 4. Variation in fluorescence intensity of diesel at (A) $\lambda_{ex} = 385\,\text{nm}$, $\lambda_{em} = 415\,\text{nm}$, (B) $\lambda_{ex} = 435\,\text{nm}$, $\lambda_{em} = 470\,\text{nm}$, (C) $\lambda_{ex} = 475\,\text{nm}$, $\lambda_{em} = 600\,\text{nm}$ and (D) sum of the intensity at B & C with concentration obtained by TSF measurement. Arrow indicates that below 16% v/v of diesel concentration resonance energy transfer from PAC of 3 to 4 member ring PACs is the dominant factor, at above 58%, v/v of diesel concentration self-quenching of 6 member ring PAC dominates and in between 16 to 58%, v/v of diesel concentration resonance energy transfer from 5 to 6 member ring PACs dominates.

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seen earlier that relative concentration of lower member ring PACs is more compared to higher membered ring PACs, and now we observed that self-quenching is also a dominating factor for higher membered ring PACs. Therefore, the rate of self-quenching increases with decrease in PACs ring size. Hence the fluorescence for neat diesel sample at lower excitations ($\lambda_{ex} \sim 250\,\text{nm}$) gets totally quenched due to self-quenching and surface geometry effect[13]. The dominance of self-quenching of higher membered ring PACs at higher concentration ($>54\%$ v/v, Fig. 4) also explains the flatness of Figure 3a at higher concentration.

Effect of Solvent

The plot of ϕ_F^T value of diesel in different solvent is shown in Fig. 5, which shows an increment in ϕ_F^T value with solvent polarity. This indicates that there is an interaction between the fluorophores (PACs) and solvent molecules during dilution[17]. Hence, red shift of $\lambda_{ex}^{max}/\lambda_{em}^{max}$ with concentration of diesel is partly due to variation in solvent polarity during various dilutions. Therefore, the change in relative energy transfer of diesel is mainly

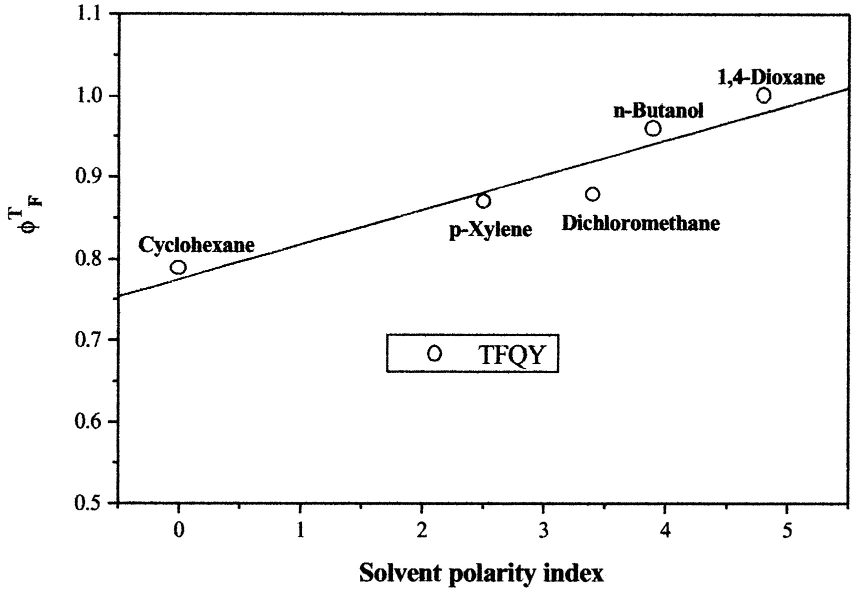
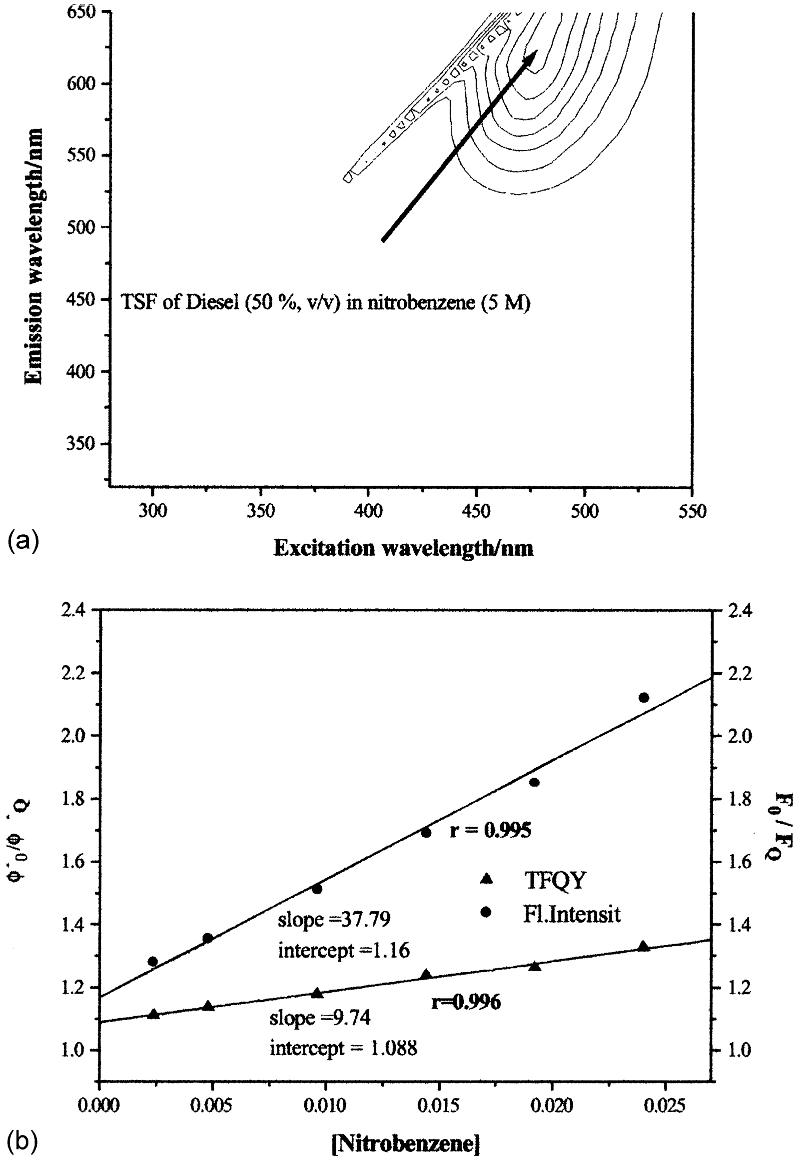


Figure 5. Variation of total fluorescence quantum yields (ϕ_F^T) of diesel with different solvents (50%, v/v).



(a)

(b)

Figure 6. (a) TSF contour map of diesel in presence of 5 M nitrobenzene (50%, v/v) (scattering uncorrected spectrum), (b) Stern-Volmer plot of diesel in presence of various concentration of nitrobenzene by total fluorescence quantum yield measurement (ϕ_0^T/ϕ_Q^T) and by fluorescence intensity measurement (F_0/F_Q) at $\lambda_{ex} = 435$ nm, $\lambda_{em} = 470$ nm. Subscript 0 and Q indicate without and with nitrobenzene respectively.

due to the phenomenon like resonance energy transfer from the higher to lower member ring PACs and partly due to solvent polarity of the medium with various dilutions.

Selective Fluorescence Quenching

Selective fluorescence quenching is a powerful method to selectively determine the target molecule by eliminating fluorescence from undesired molecule[18,19]. As nitrobenzene is known to be a good quencher molecule for most of the PACs[20], we have tested nitrobenzene as a selective fluorescence quencher molecule for PACs in diesel. Interestingly, it is observed that except the higher emission band ($\lambda_{ex} = 475\,\text{nm}$, $\lambda_{em} = 600\,\text{nm}$) of diesel all other fluorescence got totally quenched by 5 M nitrobenzene (50% v/v), which was slightly affected by 5 M nitrobenzene (Figure 6a). The quantitative evaluation of selective quenching of PACs in diesel by nitrobenzene has been done by ϕ_F^T and fluorescence intensity measurement (Figure 6b). It is noticed that for various quencher concentration (0 to 0.025 M), both the Stern-Volmer plot obtained from fluorescence intensity ($\lambda_{ex} = 435\,\text{nm}$ & $\lambda_{em} = 475\,\text{nm}$) and ϕ_F^T measurement show good linearity ($r = 0.995$ & 0.996, respectively). On the other hand, the fluorescence intensity measurement at $\lambda_{ex} = 475\,\text{nm}$ and $\lambda_{em} = 600\,\text{nm}$ shows a 5% variation without a systematic trend in the given nitrobenzene concentration. This 5% variation might be due to the change in fluorescence intensity by resonance energy transfer and inner filter effect from lower to higher member ring PACs.

The study shows that in diesel the relative concentration of PACs decreases with the aromatic ring size, consequently, at too dilute conditions higher member ring PACs lose their sensitivity. It is also observed that resonance energy transfer from lower to higher membered ring PACs and self-quenching via solvent collision of PACs at higher concentration are dominant factors in diesel, whereas solvent polarity plays a minor role. Total fluorescence quantum yield measurement can be used to check diesel contamination. Nitrobenzene is found to be a selective fluorescence quencher for PACs present in diesel.

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