ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 94 (1996) 53–62

Journal of PHOTOCHEMISTRY AND PHOTOBIOLOGY A: CHEMISTRY

Charge transfer and fluorescence behaviour of hexylamine and 7,7,8,8-tetracyanoquinodimethane in compartmentalized (reverse micelle and microemulsion) and non-aqueous environments

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Received 6 February 1995; accepted 25 August 1995

Abstract

The charge transfer interaction between hexylamine (HA) and 7,7,8,8-tetracyanoquinodimethane (TCNQ) and the fluorescence behaviour of the charge transfer complex were studied in non-aqueous solvents (dichloromethane, chloroform, carbon tetrachloride, heptane, iso-octane, decane and cyclohexane) and in sodium bis(2-ethyl-hexyl)sulphosuccinate (AOT)–cyclohexane reverse micellar medium and water–AOT–cyclohexane microemulsion medium. A 1:1 charge transfer complex between HA and TCNQ was formed, and its binding strength was estimated by the Benesi–Hildebrand equation. The charge transfer complex was fluorescent; this was hindered by AOT and by a higher concentration of HA. The results were analysed using the Stern–Volmer equation. At a constant [water]/[AOT] mole ratio (ω), the charge transfer and quenching processes increased and decreased respectively with increasing [AOT]. At constant [AOT], both phenomena were enhanced with increasing ω. The photophysical processes were influenced by the water–oil interface containing AOT; in contrast, the medium polarity had no influence.

Keywords: Charge transfer; Fluorescence; Hexylamine–TCNQ; Reverse micelles; Microemulsions; Non-aqueous environments

1. Introduction

The compartmentalized environments formed by the aggregation of amphiphiles, as in reverse micelles and microemulsions, possess interesting catalytic and solubilizing properties [1–5]; they can also act as membranes for the transport of solutes [6,7]. Investigations to determine their physicochemical properties, including energetics of formation, stability, chemical and biological reaction equilibria [8–10] and kinetics [11–15], have been performed.

In the compartmentalized condition, the core water and amphiphilic interface exhibit certain physical states and can influence, in a specific manner, the physicochemical processes occurring therein. Photophysical processes, e.g. fluorescence, phosphorescence, luminescence, electron transfer (or charge transfer), etc., show interesting properties in the compartmentalized condition and have been studied in detail [16–22].

However, investigations on the charge transfer (CT) interaction in micellar media, particularly reverse micellar and microemulsion media, are limited. Examination of such interactions at the liquid–liquid, liquid–solid and air–liquid interfaces has been performed recently [23].

CT complexation may play an important role in biological systems [24], and the functionality of bioactive compounds may depend on their ability to form molecular complexes with bioreceptors [25]. A special role of the interface in such processes is envisaged. The study of the CT interaction in compartmentalized liquids is expected to offer insight into the understanding of such interactions in biological systems.

To this end, we have undertaken a spectrophotometric study of the CT interaction between hexylamine (HA) and 7,7,8,8-tetracyanoquinodimethane (TCNQ) in different non-aqueous solvents as well as in reverse micelles and microemulsions formed with the versatile surfactant Aerosol-OT (AOT) (sodium bis(2-ethyl-hexyl)sulphosuccinate), water and cyclohexane. We have also studied the fluorescence characteristics of the CT complex in the compartmentalized condition. TCNQ has been used to probe the kinetics of solubilization [26] and to characterize micelles by CT interaction with surfactants [27,28]. HA is a potent cosurfactant used in the formation of microemulsions [29]. In the present system,

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HA acts as the donor forming a CT complex with the acceptor TCNQ.

2. Experimental details

2.1. Materials

TCNQ and HA were obtained from Sigma (USA) and Fluka (Germany) respectively. TCNQ was recrystallized from acetonitrile and the purity of the product was checked by melting point (m.p.) measurements. The surfactant (AOT) (tested product of Sigma, USA) was the same sample as used previously [10,30]. The oils cyclohexane (Cy), heptane (Hp), decane (Dc) and iso-octane (i-Oc) were also the same as used previously [10]. The other non-aqueous solvents (CH_2Cl_2, $CHCl_3$ and CCl_4) were spectrograde products of BDH (UK) or E. Merck (Germany). They were purified and dried following standard procedures.

2.2. Measurements

Absorption measurements were taken using a Shimadzu (model 160A) UV–visible spectrophotometer with matched quartz cells of 0.5 cm path length. Emission spectra were recorded with a Hitachi fluorescence spectrophotometer (model F 4010) using emission and excitation slit widths of 5 nm each and quartz cuvettes of 1 cm path length. Freshly prepared solutions were used in all experiments.

2.3. Spectral measurements

A measured volume of the stock solution of TCNQ (prepared by dissolving in chloroform) was evaporated nearly to dryness and to this was added a requisite aliquot of HA using a microsyringe. The complex thus formed between HA and TCNQ was then taken in different media, namely Cy, Hp, Dc, i-Oc, halomethanes, reverse micellar and microemulsion media, for spectrophotometric measurements. All the solutions were prepared at room temperature and were given 1 h to equilibrate. Absorption spectral measurements were taken at 295 ± 0.5 K. All runs were duplicated and the mean values were used for data processing and analysis.

3. Results and discussion

3.1. CT interaction

The absorption spectrum of TCNQ in Cy exhibited a maximum at 396 nm (inset, Fig. 1). A new band, around 430 nm,

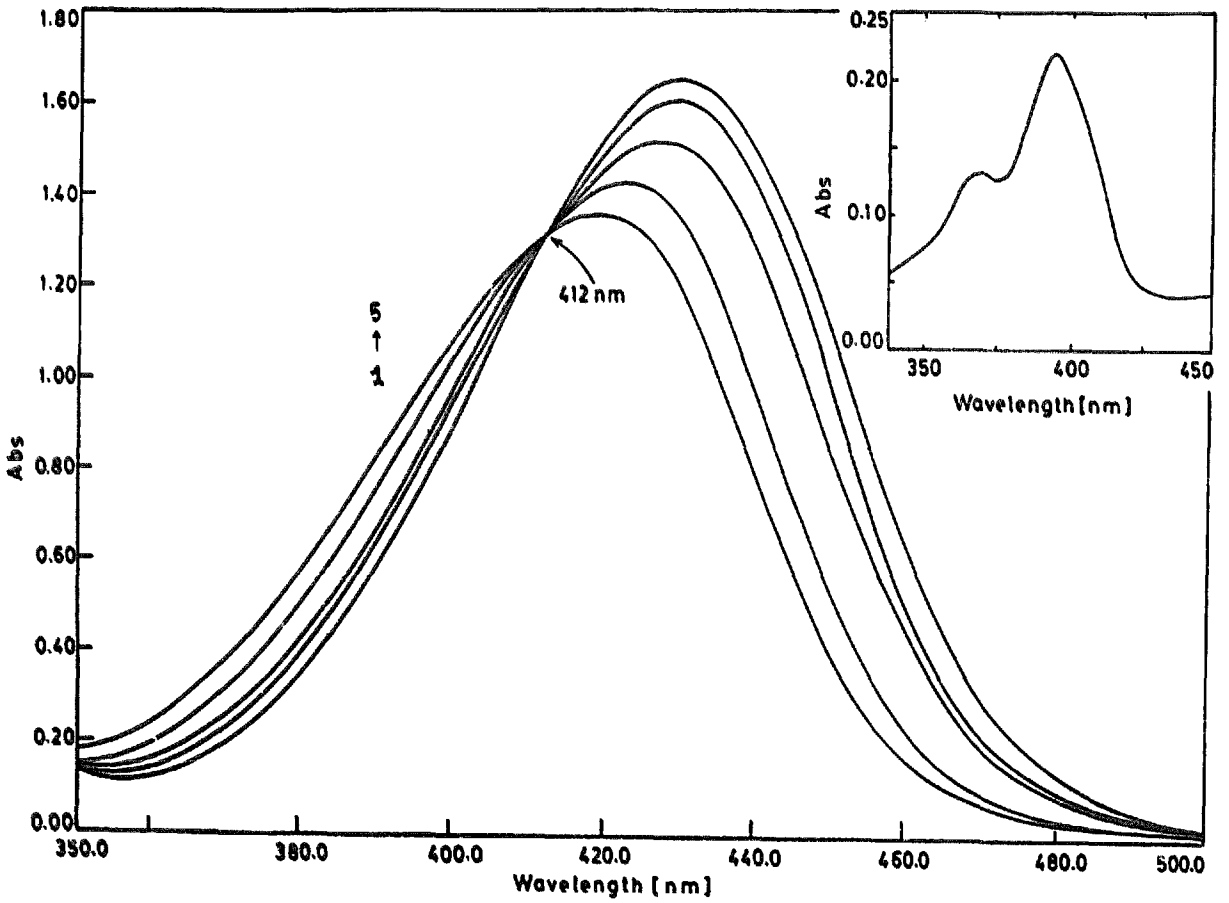

Fig. 1. Absorption spectra of TCNQ–HA in Cy ([TCNQ] = 72.1 μmol dm^{-3}). Curves 1–5: [HA] is 0.11, 0.17, 0.34, 0.51 and 0.68 mol dm^{-3} respectively. Inset: absorption spectrum of TCNQ in Cy ([TCNQ] = 50 μmol dm^{-3}).

attributed to the CT band, was obtained for a solution of TCNQ and HA in Cy medium, using the reagents, except TCNQ, as control. The absorption maximum suffered a small bathochromic shift with increasing [HA]. The spectra of TCNQ–HA at fixed [TCNQ] and varying [HA] in Cy are illustrated in Fig. 1. The intensity of absorption increased with increasing [HA]. An isosbestic point at 412 nm indicated 1:1 complex formation.

In the presence of AOT, TCNQ also formed a CT complex with HA in Cy medium. The CT band appeared at 432 nm, without a bathochromic shift with increasing [HA]; the intensity of absorption increased with increasing [HA] (Fig. 2(A)). According to a previous report [27c], TCNQ forms a CT complex with AOT (where AOT is the electron donor) with four bands at 480, 680, 750 and 850 nm. We observed five bands at 398, 467, 685, 741 and 847 nm as shown in Fig.

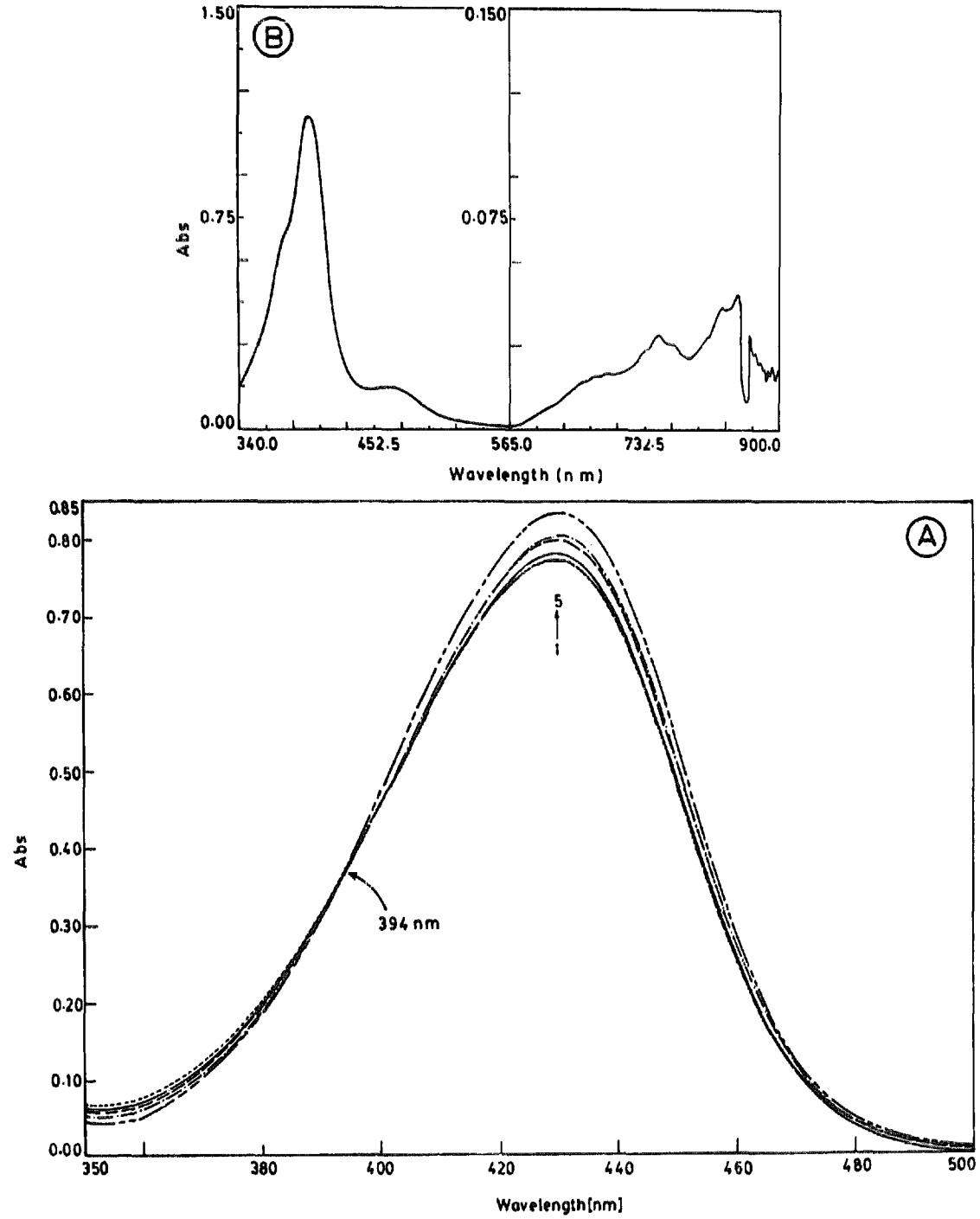

Fig. 2. (A) Absorption spectra of TCNQ–HA in AOT–Cy reverse micelle. [TCNQ] = 50 μmol dm^{-3}, [AOT] = 6.25 mmol dm^{-3}. Curves 1–5: [HA] is 0.11, 0.23, 0.34, 0.45 and 0.56 mol dm^{-3} respectively. (B) Absorption spectrum of TCNQ in the presence of [AOT] = 100 mmol dm^{-3} ([TCNQ] = 50 μmol dm^{-3}).

2(B) for the TCNQ–AOT system. The [AOT]-dependent absorption of the TCNQ–HA system is presented in Fig. 3(A). For a given set of solutions of fixed [TCNQ] and varying [HA], the absorbance increased with increasing AOT up to 0.1 mol dm^{-3} and reached a plateau; at [AOT] = 0.2 mol dm^{-3}, all the curves virtually merged to a single point. At lower [AOT] (less than 8 mmol dm^{-3}), the effect of [HA] on the absorption was significant. A similar observation of an increased absorbance of the TCNQ–AOT CT complex in chloroform with increasing amphiphile concentration was reported [27c,31]. The phenomenon was conveniently employed in the determination of the critical micelle concentration (CMC) of surfactants [27b,27c,28].

The absorption spectra of the TCNQ–HA CT complex in water–AOT–Cy microemulsion medium at three [water]/[AOT] mole ratios (ω) of 4.2, 6.9 and 9.7 at [AOT] = 0.1 mol dm^{-3} were recorded, and the CT band appeared at 425 nm without any bathochromic shift (spectra not shown). The absorbance increased with increasing [HA] at all ω values, but decreased with increasing ω for given [TCNQ] and [HA] values (Fig. 3(B)). A large decrease in intensity was observed at [HA] ≈ 0.34 mol dm^{-3}. It has been reported [5,32] that the spectral intensity of an absorbing or emitting species is enhanced in AOT reverse micelles (microemulsions) at low water contents, particularly at $\omega < 6$. In such conditions, the water molecules remain bound to the AOT anion and the counter-cation Na^+ making the photoactive species free to exhibit its full characteristics. At higher ω, free water molecules reduce the photophysical activity by the process of quenching [5,32].

3.2. Quantification of CT complexation

The equilibrium constant (K_c) and molar absorbance (ϵ_c) of the CT complex between TCNQ and HA were calculated using the Benesi–Hildebrand equation [33]

$$\frac{[C_a]}{A} = \frac{1}{\epsilon_c} + \frac{1}{K_c \epsilon_c} \frac{1}{[C_b]} \quad (1)$$

where $[C_a]$ and $[C_b]$ are the concentrations of the acceptor (TCNQ) and donor (HA) respectively and A is the absorbance of the solution. The ϵ_c and K_c values were evaluated from the intercept and slope of the linear plot between $[C_a]/A$ and $[C_b]^{-1}$. A representative presentation is shown in Fig. 4 and the K_c and ϵ_c values are given in Table 1. The K_c values in different media follow the order: reverse micelle of AOT (0.1 mol dm^{-3}) ≫ reverse micelle of AOT (6.25 mmol dm^{-3}) > water–AOT–Cy ($\omega = 9.7$) > water–AOT–Cy ($\omega = 6.9$) > water–AOT–Cy ($\omega = 4.2$) > Cy. The CT complex is least stable in Cy. The molar absorbances (ϵ_c) are in the order: Cy > reverse micelle > microemulsion. The K_c values do not vary according to the polarity of the medium, although Mulliken's CT theory [34] suggests that K_c should increase with increasing polarity of the medium [35]. The order of polarity for the presently studied media is: microemulsion > reverse micelle > Cy. The ϵ_c values are hardly dependent on the [AOT] value in reverse micelles, whereas in microemulsion, ϵ_c decreases with increasing ω.

To explore the effect of polarity on the CT complex of TCNQ–HA, the interaction was also studied using different

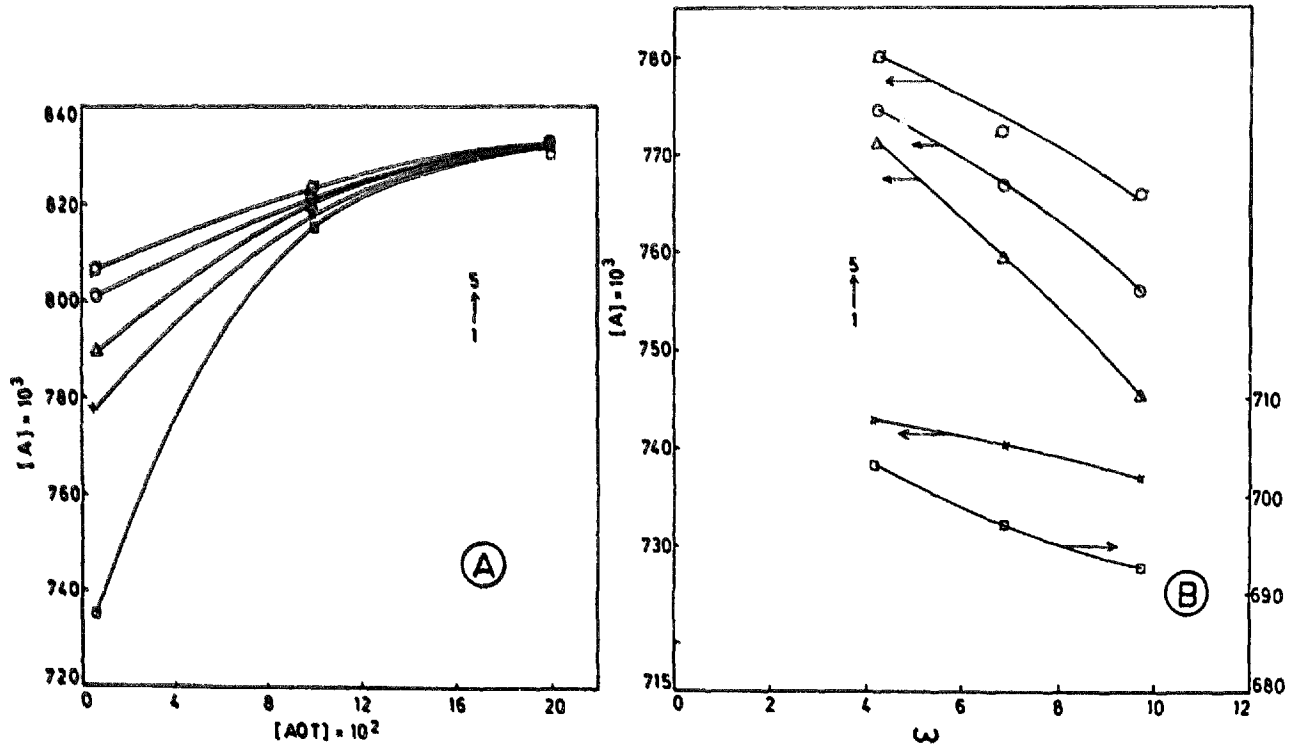

Fig. 3. (A) Plot of [AOT] vs. absorbance of TCNQ–HA at [TCNQ] = 50 μmol dm^{-3}. Curves 1–5: [HA] is 0.11, 0.23, 0.34, 0.45 and 0.56 mol dm^{-3} respectively. (B) Plot of ω vs. absorbance of TCNQ–HA at [TCNQ] = 50 μmol dm^{-3}. Curves 1–5: [HA] is the same as in (A).

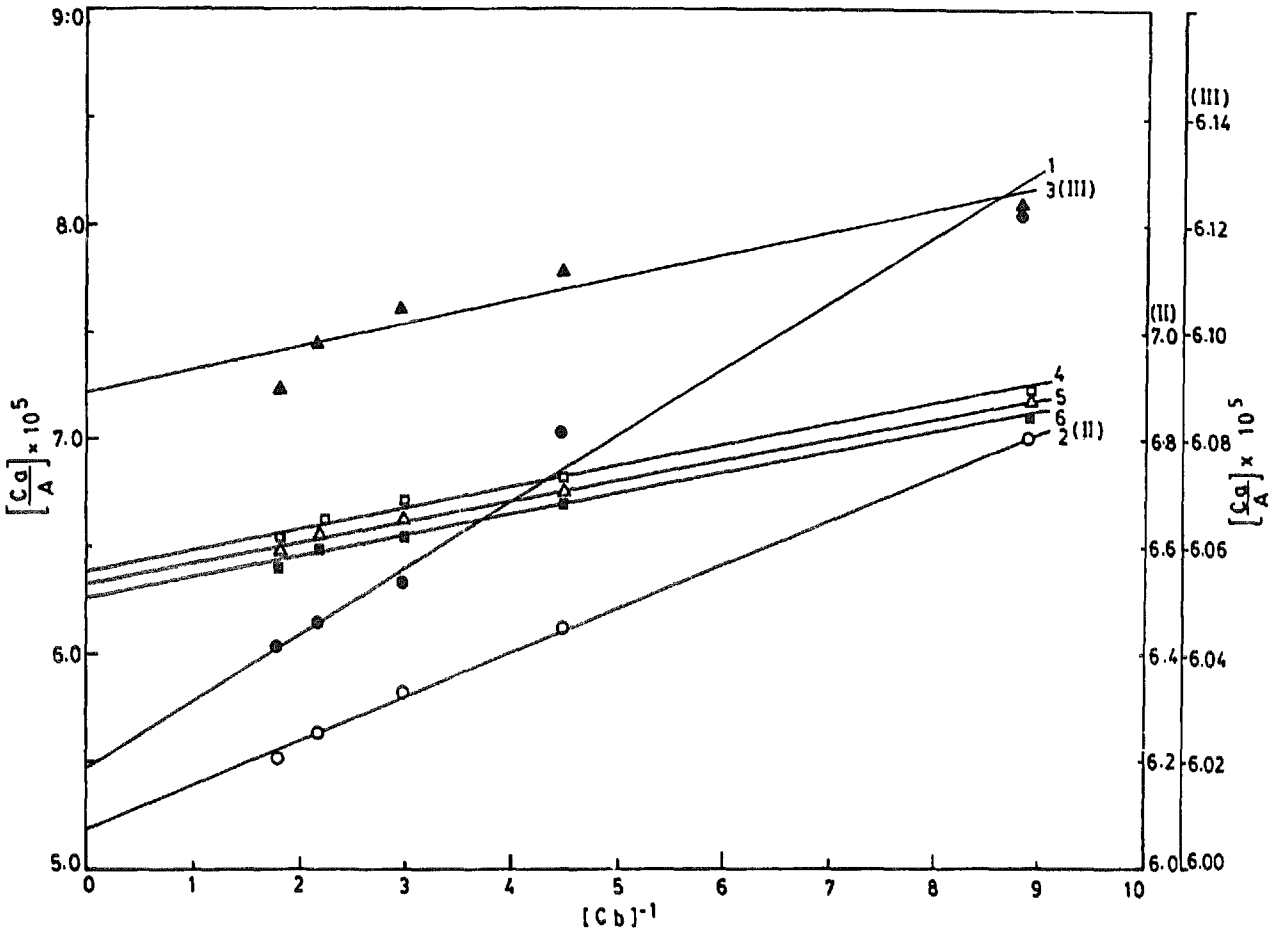

Fig. 4. Plot of the Benesi–Hildebrand equation for TCNQ–HA in different media. Curves 1–6: Cy; AOT–Cy (6.25 and 100 mmol dm^{-3} AOT); water–AOT–Cy microemulsions (ω = 4.2, 6.9 and 9.7). [TCNQ] = 50 μmol dm^{-3}.

non-aqueous solvents, namely CH_2Cl_2, $CHCl_3$, CCl_4, Cy, Hp, i-Oc and Dc (Fig. 5(A)). The λ_{max} value obtained was 424 ± 2 nm in all cases, but the absorbances varied in the order: $CHCl_3$ > CH_2Cl_2 > Cy > Dc > i-Oc > Hp. The observed spectral characteristics and the dielectric constants of the media are summarized in Table 2. The absence of a straightforward correlation of the results with the solvent polarity may be due to back coordination, as proposed in the Dewar–Lepley molecular orbital theory [36], and the specific solvation of the species involved, as proposed by Carter et al. [37]. Cipiciani et al. [35] explained the anomalous solvent effect on CT complexation in CCl_4 by following the theory of Merrifield and Philips [38] and Ewall and Sonnessa [39], who reported that TCNE also forms a complex with the solvents (CH_2Cl_2 and $CHCl_3$).

3.3. Fluorescence emission of the CT complex

The fluorescence spectra of the TCNQ–HA CT complex ([TCNQ] = 50 μmol dm^{-3} and [HA] = 0.23 mol dm^{-3}) at 295 K in different non-aqueous solvents are presented in Fig. 5(B). The complex excited at 424 nm emitted a maximum around 500 nm in CCl_4, i-Oc, Hp, Dc and Cy, and at 570 nm and 565 nm in CH_2Cl_2 and $CHCl_3$ respectively. The spectra were symmetric with an appreciable Stokes shift. The emission band was broad in CCl_4; the order of intensity in the

Table 1
Molar extinction coefficient (ϵ_c) and stability constant (K_c) of CT complex in different media at 295 K

Medium	[AOT] (mmol dm^{-3})	ω	$\epsilon_c \times 10^{-4}$ (dm^3 mol^{-1} cm^{-1})	K_c (dm^3 mol^{-1})
Cy	0	0	2.41	20.30 (0.9909)
AOT–Cy	6.25	0.74	1.65	72.17 (0.9990)
AOT–Cy	100	0.74	1.64	1104 (0.8800)
W–AOT–Cy	100	4.2	1.60	64.31 (0.9953)
W–AOT–Cy	100	6.9	1.59	65.90 (0.9609)
W–AOT–Cy	100	9.7	1.56	68.97 (0.9941)

W, water. Values in parentheses are the correlation coefficients of regression analysis.

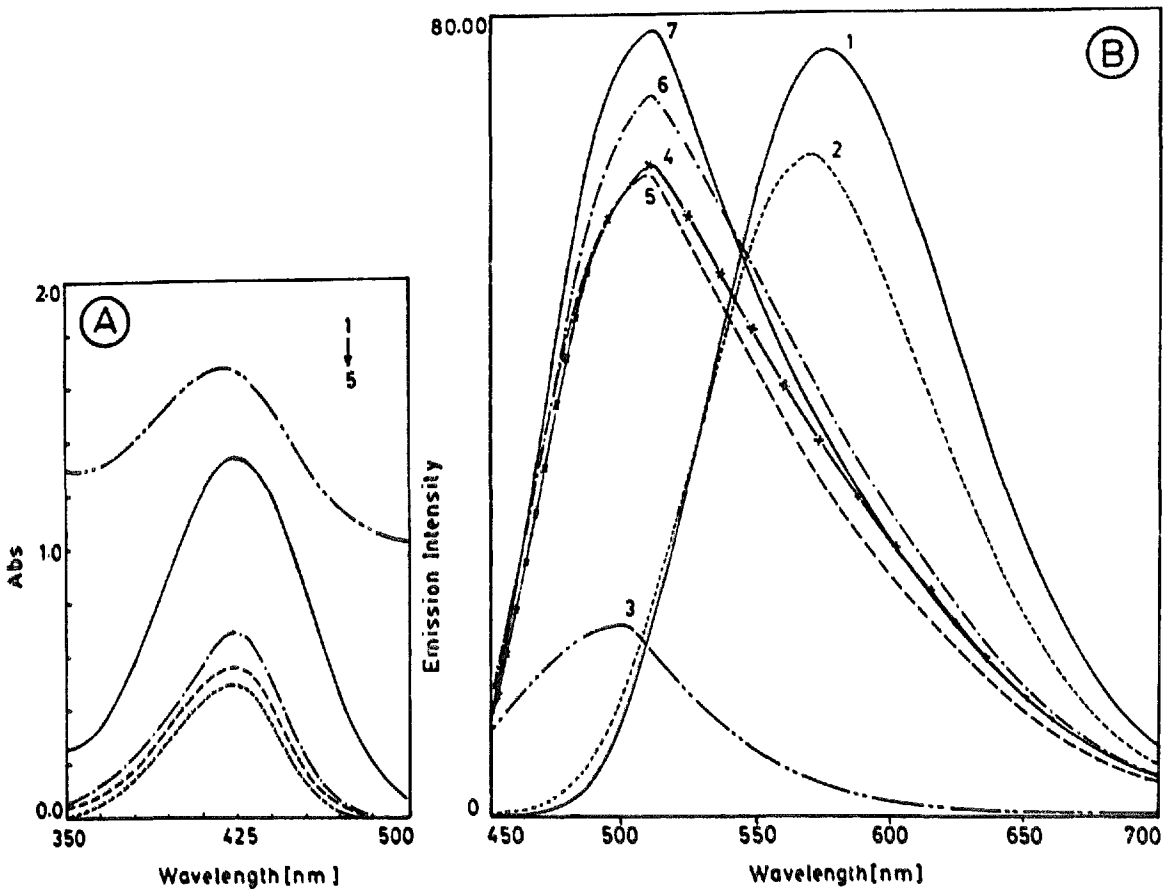

Fig. 5. (A) Absorption spectra of TCNQ–HA in different non-aqueous solvents. Curves 1–5: $CHCl_3$, CH_2Cl_2, Cy, i-Oc and Hp respectively. [TCNQ] = 50 μmol dm^{-3} and [HA] = 0.23 mol dm^{-3}. (B) Emission specra of TCNQ–HA in different non-aqueous solvents. Curves 1–7: CH_2Cl_2, $CHCl_3$, CCl_4, Hp, i-Oc, Dc and Cy respectively. [TCNQ] and [HA] are the same as in (A).

Table 2
Absorption and emission characteristics of CT complex in different non-aqueous solvents at 295 K

Solvent	Dielectric constant	Absorption		Emission	
		λ_{max} (nm)	Absorbance	λ_{max} (nm)	Intensity
CH_2Cl_2	9.08	424.4	1.344	565.2	76.2
$CHCl_3$	4.80	418.3	1.675	560.4	65.8
CCl_4	2.24	–	–	497.6	19.0
Hp	1.98	423.5	0.495	501.2	64.8
i-Oc	1.96	422.5	0.562	501.6	63.8
Dc	1.99	426.3	0.632	502.0	71.8
Cy	2.02	425.0	0.733	500.6	78.2

media was: $CCl_4 \ll$ i-Oc < Hp < $CHCl_3$ < Dc < CH_2Cl_2 < Cy.

The emission spectra of the CT complex in Cy, AOT–Cy reverse micelles and water–AOT–Cy microemulsion ($\omega = 9.7$) were recorded; the effect of [AOT] on the emission spectrum of a solution of fixed [TCNQ] and [HA] was also studied. On excitation of the CT system at 430, 432 or 425 nm, a broad, structureless, mirror-symmetric fluorescence band [23], with a maximum around 500 nm and a large Stokes shift of 70 nm, was observed. A representative spectral pattern is presented in Fig. 6.

According to Mulliken and Person [40], the potential minimum of the CT excited state (mainly governed by the $D^+...A^-$ interaction) does not coincide with that of the ground state (governed mainly by the D...A interaction). The internuclear distance R_{DA}, and hence the potential energy curve, of the excited state is different from that of the CT ground state. Thus the emission spectrum (a result of the

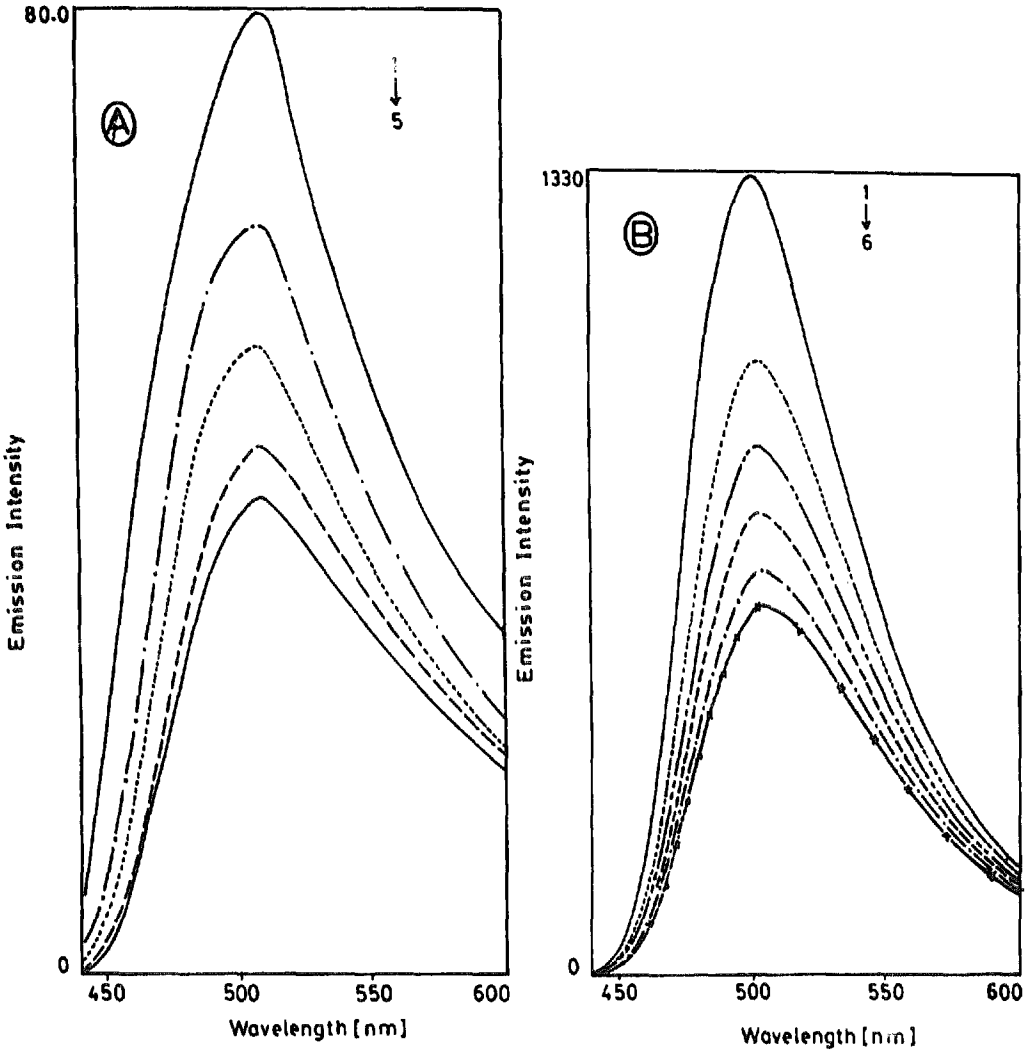

Fig. 6. (A) Emission spectra of TCNQ–HA in Cy medium (excited at 430 nm). Curves 1–5: [HA] is the same as in Fig. 2(A). [TCNQ] = 50 μmol dm^{-3}. (B) Representative emission spectra of TCNQ–HA at [AOT] = 100 mmol dm^{-3} (excited at 432 nm); [TCNQ] = 50 μmol dm^{-3}. Curves 1–6: [HA] is 0.04, 0.11, 0.23, 0.34, 0.45 and 0.56 mol dm^{-3} respectively.

Franck–Condon transition from an essentially ionic state with high binding energy) of the CT complex should show a large bathochromic shift with respect to that of the absorption spectrum (caused by the Franck–Condon transition from an essentially neutral state with low binding energy) [23].

Examination of Figs. 6(A) and 6(B) shows that the emission band in Cy medium exhibits a red shift of about 6 nm with increasing [HA], whereas in AOT–Cy reverse micellar medium the band appears at 503 nm. In water–AOT–Cy microemulsion medium, the emission band is at 506 nm, independent of ω.

The fluorescence intensity depends on the environment. In reverse micellar medium, it is 4–7-fold higher than that in microemulsion medium and about 12-fold higher than that in Cy medium. For [TCNQ] = 50 μmol dm^{-3}, the fluorescence intensity increases with HA addition up to 19 mmol dm^{-3}, and thereafter decreases. This is due to quenching of the CT complex emission by [HA] [41], an external quencher not being necessary. We consider that, at higher [HA], the $HA^+...TCNQ^-$ complex reacts with a second HA establishing the following equilibrium

$$(HA^+\cdots TCNQ^-) + HA \overset{K_{SV}}{\rightleftharpoons} (H^+\cdots TCNQ^-)\cdots HA \quad (2)$$

with a reduction in the emission potential of the CT complex. Here K_{SV} is the well-known Stern–Volmer [42] constant.

3.4. Quantification of the fluorescence behaviour

The Stern–Volmer plots (Fig. 7(A)) according to the equation

$$F_0/F = 1 + K_{SV}[Q] \quad (3)$$

where F_0/F is the relative quantum yield of fluorescence of the CT complex in the presence of amine quencher of concentration [Q], was used to evaluate the binding constant (K_{SV}). The results are presented in Table 3. Since the [HA]

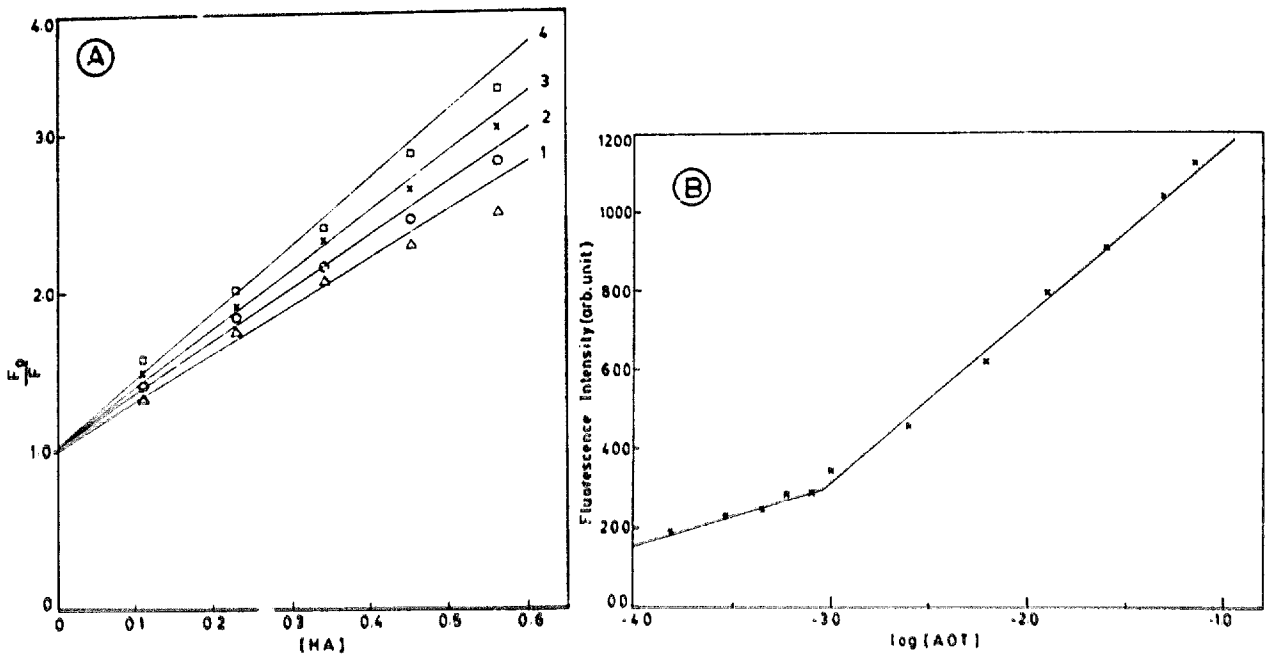

Fig. 7. (A) Stern–Volmer plot for the TCNQ–HA CT complex in water–AOT–Cy microemulsion and Cy media. Curves 1–4: $\omega = 4.2$, 6.9, 9.7, and Cy respectively. (B) Plot of log[AOT] vs. fluorescence intensity of the TCNQ–HA CT complex. [TCNQ] = 50 μmol dm^{-3} and [HA] = 0.11 mol dm^{-3}.

value used was much higher than 19 mmol dm^{-3}, its total concentration was considered to be equal to [Q]. The fluorescence intensity of the CT complex at HA = 19 mmol dm^{-3} was considered to be F_0.

3.5. Quenching in reverse micellar and microemulsion media

The fluorescence spectra of the CT complex formed between fixed [TCNQ] (50 μmol dm^{-3}) and varying [HA] (0.04–0.56 mol dm^{-3}) at four different AOT/Cy ratios were recorded on excitation at 432 nm. Sharp emission peaks at 503 nm appeared at lower [HA] values, which became broader at higher [HA] values. F increased with increasing [AOT] and finally levelled off. At [AOT] < CMC, the Stern–Volmer plot deviated from linearity on the higher side of [HA], but was satisfactorily linear at [AOT] > CMC (plots not shown). The K_{SV} values measured at 295 K are presented in Table 3. In the presence of a small amount of [AOT] = 0.8 mmol dm^{-3}, the K_{SV} value was 6.5-fold greater than that in pure Cy. Increasing [AOT] at $\omega = 0.74$ led to a decrease in K_{SV}; at 100 mmol dm^{-3}, it was lower than that in pure Cy. At [AOT] = 100 mmol dm^{-3}, an increase in ω from 0.74 to 9.7 led to a minor increase in K_{SV}. Thus a small amount of AOT assists the quenching of the complex by HA; at higher concentrations, HA interacts with AOT reducing the quenching process. The F values for the complex at fixed [TCNQ] and [HA] and varying [AOT], when plotted against log[AOT], yielded a distinct break at 0.93 mmol dm^{-3} (Fig. 7(B)). This CMC value of AOT in Cy is higher than that reported by Muto and Meguro [27c] based on the iodine solubilization method. The fluorescence spectral technique has been successfully employed for the CMC determination of surfactants [43–45].

Table 3
Stern–Volmer constant (K_{SV}) for CT complex in oil, reverse micellar and microemulsion media at 295 K

Medium	[AOT] (mmol dm^{-3})	ω	K_{SV} (mol^{-1} dm^3)
Cy	–	–	3.79 (0.9998)
AOT–Cy	0.8	0.74	28.88 (0.9997)
AOT–Cy	6.25	0.74	11.18 (0.9961)
AOT–Cy	25.0	0.74	6.51 (0.9925)
AOT–Cy	100.0	0.74	2.60 (0.9966)
W–AOT–Cy	100.0	4.2	2.89 (0.9947)
W–AOT–Cy	100.0	6.9	3.06 (0.9979)
W–AOT–Cy	100.0	9.7	3.48 (0.9984)

W, water. Values in parentheses are the correlation coefficients of regression analysis.

3.6. Process phenomenology

The results of the photophysical processes (Tables 1–3) point to the specific influence of the interface and the water pool of the reverse micelles and microemulsion. The much lower values of both K_c and K_{SV} in Cy than in the reverse micelles and microemulsion confirm the influence of compartmentalization on the photophysical processes at low ω. The limiting K_c and K_{SV} values, obtained from the plots of K_c vs. ω^{-1} and K_{SV} vs. ω^{-1} extrapolated to $\omega^{-1} = 0$, were 71.0 and 4.05 respectively. They give a measure of CT complex formation and the fluorescence quenching of the complex respectively at minimum AOT, i.e. in excess water. In the stable compartments studied, the CT [19a,32b] and flu-

orescence spectral [19a,32c] properties are governed by the interface as well as the interior of the water pool. The rotational correlation time and spin-lattice relaxation rates have shown that, in small water pools (with $[H_2O]/[Na^+] \approx 6$), the water molecules are highly immobilized by strong ion–dipole interaction with the interfacial AOT anion and the underlying Na^+ counter-ions [19a]. TCNQ [26a,27b] and HA [29] are very poorly soluble in water; TCNQ is poorly soluble in Cy and in non-aqueous solvents in general, bu: HA shows good solubility. The acceptor thus resides at the oil–water interface of reverse micelles, where the CT interaction with HA occurs. At low water content (low ω), the water molecules are not free and the hydrated AOT anion and Na^+ cation exhibit electrostatic interaction; the influence of the interface on the TCNQ–HA interaction is minor. At higher ω, the interface becomes labile, the AOT anion and Na^+ cation are separated and free water molecules are available to perturb the photophysical process [19a]. This represents a probable analysis of the complex photophysical phenomena occurring in these compartmentalized environments.

4. Conclusions

TCNQ and HA form a 1:1 CT complex in non-aqueous solvents, as well as in reverse micelles and microemulsions prepared with the amphiphile AOT; the complex is appreciably fluorescent. The fluorescence of the CT complex increases with increasing [HA] and is quenched after a threshold concentration. The complexation and quenching phenomena are not correlated with the polarity of the medium. The [water]/[AOT] composition of the comparmentalized liquid has a strong influence on the photophysical phenomena studied, which preferentially occur at the water–oil interface.

Acknowledgements

We gratefully acknowledge the help extended by the Saha Institute of Nuclear Physics (SINP), Calcutta and Professor Sanjib Ghosh (Presidency College, Calcutta) in recording the emission spectra. The technical assistance of Mrs. C. Raha (SINP) and Mr. A.K. Das (Geological Studies Unit) is also acknowledged with appreciation.

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