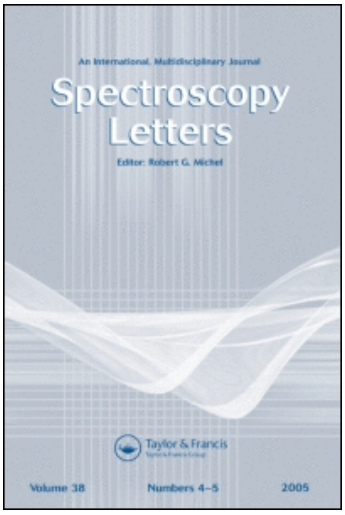

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

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To cite this Article Jiang, Yun-Bao , Jin, Min-Gang , Zhang, Yong , Du, Xin-Zhen and Huang, Xian-Zhi(1996) 'Effect of $K_4FE(CN)_6$ and $K_3FE(CN)_6$ on TICT Dual Fluorescence of Sodium p-Dimethylaminobenzoate in Cetyltrimethylammonium Chloride Micelle. Identification of the Magenetic Effect in TICT Process', Spectroscopy Letters, 29: 5, 877 — 884
To link to this Article: DOI: 10.1080/00387019608001618
URL: http://dx.doi.org/10.1080/00387019608001618

SPECTROSCOPY LETTERS, 29(5), 877-884 (1996)

EFFECT OF $K_4FE(CN)_6$ AND $K_3FE(CN)_6$ ON TICT DUAL FLUORESCENCE OF SODIUM p-DIMETHYLAMINOBENZOATE IN CETYLTRIMETHYLAMMONIUM CHLORIDE MICELLE. IDENTIFICATION OF THE MAGENETIC EFFECT IN TICT PROCESS

Keywords: Magnetic field effect, Electric field effect, TICT, Dual fluorescence, Sodium p-dimethylaminobenzoate, Micelle

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Abstract: Comparison of the effects of $K_4Fe(CN)_6$ and $K_3Fe(CN)_6$ on TICT dual fluorescence of sodium p-dimethylaminobenzoate (SDMAB) in cetyltrimethylammonium chloride (CTAC) micelle yields a conclusion that the presence of a magnetic effect unfavors the TICT process, which is

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verified by inserting the sample in a stationary magnetic field of 100G in which a decrease in the relative quantum yield of TICT state is observed.

1. Introduction

Because of the higher dipole moment of the twisted intramolecular charge transfer (TICT) state than those of the locally excited (LE) state and ground state, effect of electric field on the formation of TICT state has been theoretically expected and experimentally verified [1-6]. The magnetic effect on TICT, however, has not been examined, although that on exciplex, which is intrinsically in part and spectrally similar to those of TICT state [7, 8], has been well documented [9]. In the present letter, we will show the fisrt example for the effect of a magnetic field on TICT by a comparison of the influence of $K_4Fe(CN)_6$ and $K_3Fe(CN)_6$ as external salts on the TICT dual fluorescence of SDMAB in CTAC micelle.

SDMAB in CTAC micelle was selected as a model system since the effect of the micelle interface electric field on the TICT dual fluorescence has been established [3, 4]. The micelle interface electric field was reduced by externally introducing inorganic salt or aliphatic alcohol. For the purpose of identifying the magnetic field effect on TICT process, we select $K_4Fe(CN)_6$ and $K_3Fe(CN)_6$ as the aforementioned external salts. Because the magnetisms of the anions in $K_4Fe(CN)_6$ and $K_3Fe(CN)_6$ are different, the former being diamagnetic while the latter paramagnetic. It is then expected that the TICT fluorophore that is solubilized in $K_3Fe(CN)_6$ bound cationic micelle will experience both the reduced micelle interface electric field and the magnetic field originationg from the paramagnetic center in $K_3Fe(CN)_6$,

while that in $K_4Fe(CN)_6$ bound micelle only feel the reduced micelle interfcae electric field. Thus substraction of the effect of $K_4Fe(CN)_6$ on TICT fluorescence in micelle from that of $K_3Fe(CN)_6$ on the same system would yield the effect of a magnetic field on the TICT process.

2. Experimental

SDMAB was prepared by neutralization of the acid, p-dimethylamino-benzoic acid (DMABOA) [10] by aqueous NaOH solution. $K_nFe(CN)_6$ (n=3, 4) are of GR grade purchased from Shanghai the First Reagent Factory (Shanghai, China). CTAC was used as received from Tokyo Kasei, Japan. CTAB was an AR reagent of Shanghai the First Reagent Factory. Water was doubly deionized with a final electric conductivity of lower than 0.1 μ S/cm. Fluorescence spectra without the presence of an external stationary magnetic field were recorded on a Shimadzu RF-5000 fluorescence spectrophotometer, those under a stationary magnetic field were obtained by using a Hitachi 850 fluorescence spectrophotometer. The strength of the magnetic field is 100 Gauss. The excitation wavelength was 290 nm, and the slits for both the excitation and emission monochromotors were 5 nm. Electric conductivities were measured on a CDM 9300i electric conductivity detector (Xiamen, China), connected with a black platium elctrode with an elctode constant of 0.98. All the experiments were performed at ambient temperature (25 ± 2 ° C).

3. Results and Discussion

The TICT dual fluorescence of SDMAB in CTAC micelle as a function of $K_nFe(CN)_6$ (n=3, 4) concentration was monitored. The results are presented

in Figure 1 in the form of the dual fluorescence intensity ratio, I_a/I_b, versus charge-number corrected salt concentration. Here I_a and I_b are fluorescence intensities of TICT and LE bands, respectively. The salt concentration is corrected for the charge number in anion by multiplying the bulk salt concentration in solution with charge number. It is somewhat suprising to see in Figure 1 that $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ show practically no difference in the effect on I_a/I_b ratio of SDMAB in CTAC micelle.

The magnitudes of the effects of micelle interface electric field on the TICT dual fluorescence of SDMAB in $K_nFe(CN)_6$ (n=3, 4) bound CTAC micelles were evaluated by electric conductivity measurements. Thus the conductivities of $K_nFe(CN)_6$ and $K_nFe(CN)_6$ plus CTAC micelle systems (n=3, 4) were measured. In the two kinds of systems the conductivity was observed to be proportional to $K_nFe(CN)_6$ concentration. Here we difine that the slopes for the straight lines of conductivity versus salt concentration for salt and salt plus micelle systems are k_1 and k_2, respectively. It was noted that k_2's were lower than k_1's, and k_1/k_2 ratio was higher in $K_4Fe(CN)_6$ plus CTAC micelle system (2.89) than in $K_3Fe(CN)_6$ plus CTAC micelle and that the interaction between $K_4Fe(CN)_6$ and CTAC micelle is stronger. Here we should recognize tmicelle system (2.17). This is an indication that both salts interact with CTAC hat the contribution to this difference in the interaction of salt with micelle by the difference in the charge numbers in anions of two salts is corrected by employing the k_1/k_2 ratio. Therefore a more appreciable reduction in the CTAC micelle interface electric field is expeccted in $K_4Fe(CN)_6$/CTAC micelle system than that in $K_3Fe(CN)_6$/CTAC micelle system. According to our previous results on the relationship between this k_1/k_2 ratio and the decreasing rate of I_a/I_b with salt

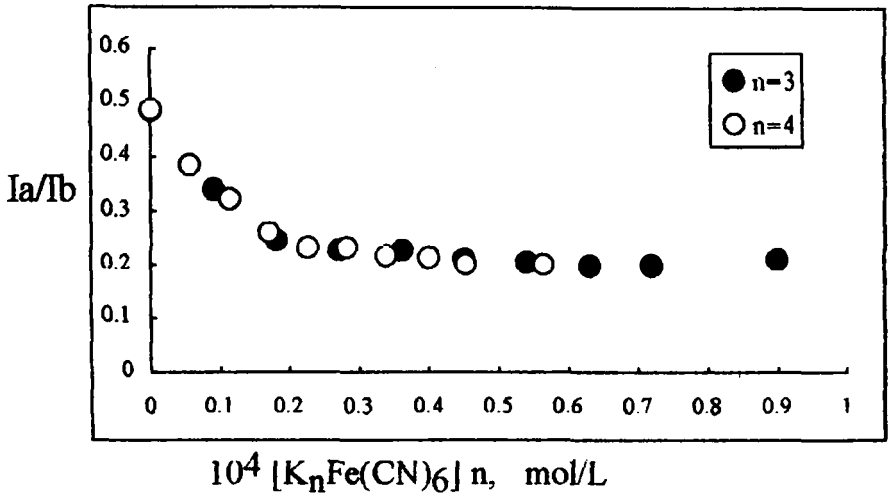

Figure 1 I_a/I_b ratio of SDMAB in $K_nFe(CN)_6$/CTAC micelle solution as a function of charge-number corrected $K_nFe(CN)_6$ concentration (n=3, 4)
SDMAB concentration is 1.25×10^{-5} mol/L. CTAC concentration is 1.5×10^{-3} mol/L.

concentration for TICT fluorophore in salt bound micelle[3], a more appreciable decrease in the I_a/I_b ratio of SDMAB in CTAC micelle by $K_4Fe(CN)_6$ than by $K_3Fe(CN)_6$ should be observed at each charge-number corrected salt concentration. Thus the curve of I_a/I_b versus corrected $K_4Fe(CN)_6$ concentration, as a whole, should be lower, if only electric field effect is present. As is seen in Figure 1, however, the fact is not the case. We practically observed the same effect for charge corrected $K_4Fe(CN)_6$ as that of $K_3Fe(CN)_6$, suggesting the presence of a magnetic effect in TICT process in $K_3Fe(CN)_6$ bound CTAC micelle. The presence of a micro-magnetic field in $K_3Fe(CN)_6$ disfavors the TICT process of SDMAB in the

complex-bound-CTAC micelle and decreases its Ia/Ib ratio, making charge-corrected effects of $K_nFe(CN)_6$ (n=3, 4) the same.

In order to check this conclusion, the dual fluorescence of SDMAB in CTAB and CTAC micelles is examined in an external magnetic field of about 100 Gauss. The fluorescence spectra are presented in Figure 2. As is seen in Figure 2, the presence of an external stationary magnetic field decreases the relative quantum yield of TICT emission or I_a/I_b ratio. This is the same as the aforementioned observation by taking $K_3Fe(CN)_6$ as an internal magnetic field [11, 12]. It is interesting to note that the decrease in I_a/I_b ratio is more appreciable in CTAB micelle (-8.38%) than in CTAC micelle (-6.61%). Same order was also observed for another TICT fluorophore, sodium diethylamino-benzoate (SDEAB) in these two micelle, -8.47% in CTAB micelle and -5.79% in CTAC micelle. The diploe moment of the TICT state of SDEAB has been demonstrated to be higher than that of SDMAB [13]. Therefore it seems to be the case that the magnetic field effect may couple with electric field effect and have nothing to do with the dipole moment difference between the TICT state and the ground state.

It is also important to point out that the same effect was observed for TICT process by using both the internal and external magnetic fields. This is different from the case in exciplex. For exciplex emission, the internal magnetic field effect [9, 14, 15] is opposite to the external magnetic effect [9, 16], the former quenching the exciplex emission whereas the latter enhancing. It appears not easy to rationalize this difference. Since, according to the exciplex and TICT models [7, 8], the cationic and anionic radicals in both

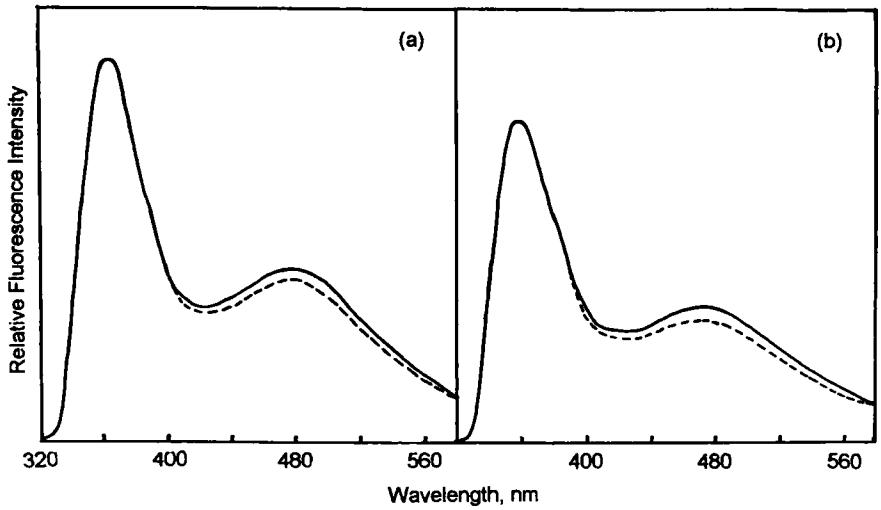

Figure 2 Fluorescence spectra of SDMAB in CTAC (a) and CTAB (b) micelles in the absence (—) and presence (- - -) of an 100 Gauss external stationary magnetic field SDMAB concentration is 2..5x10^{-5} mol/L. Both CTAC and CTAB concentrations are 2.0x10^{-3} mol/L.

states are uncoupled. Thus this difference should mean that the mechanisms that magnetic field affects TICT and exciplex emissions and/or the couplings of cationic and anioic radicals in the TICT state and in exciplex are different. Thus it may be the case that in the TICT state the cationic and anionic radicals are practically somewhat coupled, not the same as the TICT model [8] stated that the radicals are uncoupled.

ACKNOWLEDGMENTS

The financial support of this work by the National Natural Science Foundation of China through grant 29303023 is gratefully acknowledged.

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RECEIVED: January 3, 1996
ACCEPTED: February 15, 1996