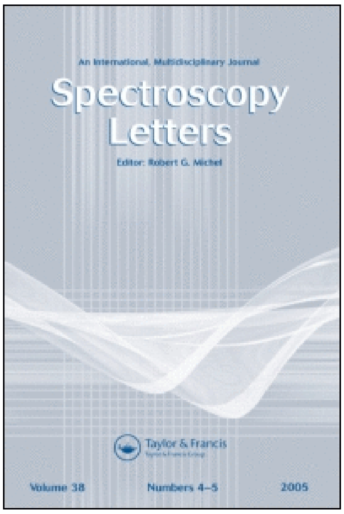

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Magneto-optic Fluorescence Behavior of Anthracene and Its Derivatives in a Diluted Magnetic Fluid Solution.

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To cite this Article Fujiwara, Kitao , Kato, Tomomi , Ito, Seiji and Takeda, Kazuhiko(1997) 'Magneto-optic Fluorescence Behavior of Anthracene and Its Derivatives in a Diluted Magnetic Fluid Solution.', Spectroscopy Letters, 30: 6, 1135 — 1147

To link to this Article: DOI: 10.1080/00387019708006712

URL: http://dx.doi.org/10.1080/00387019708006712

SPECTROSCOPY LETTERS, 30(6), 1135-1147 (1997)

Magneto-optic Fluorescence Behavior of Anthracene and Its Derivatives in a Diluted Magnetic Fluid Solution.

Key words

magnetic field, fluorometry, fluorescence, anthracene, magnetic fluid.

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Abstract

Variations in the fluorescence in the intensities of anthracene derivatives under a magnetic field were investigated in the presence of a dilute magnetic fluid. When excitation was carried out with light that was polarized parallel to the magnetic field, the intensity of the fluorescence that was polarized paralell to the magnetic field decreased by about 10 %. Although the fluorescence intensities of most of the anthracene derivatives showed a similar decrease in magnitude, that of 9,10-dimethylanthracene showed a large decrease. On the other hand, fluorescence increased when excitation and fluorescence were perpendicular to the magnetic field. The obtained phenomena can be explaned by the formation of anisotropic assembly of magnetic fluid particles in the solution.

INTRODUCTION

Magnetic fluid is used for magnetic seals, sorters, dampers , actuators, grinders, sensors and the magnetic shielding. The analysis of the composition of a sol in a magnetic fluid and its characterization are important for the uses of magnetic fluid. Recently, Nomizu et al. of Nagoya University proposed magneto-chromatography as a potential method for analyzing the composition of magnetic particles in sol. Although they did not demonstrate the efficiency of their proposed method in their report, it does seem to hold promise as an analytical tool. Very little information is available regarding the characteristics of magnetic fluid: only thin film of magnetic fluid have been observed. This is simply because normal optical methods of analysis are not applicable to opaque samples. Nevertheless, attempts have been made to elucisate the nature of magnetic fluid. For example, Taketomi investigated the birefringence of a thin film of magnetic fluid (about 10-μm thick).[2-5] In addition, one of the authors of this paper (K.F.) made a liquid-core optical fiber which holds diluted magnetic fluid. This fiber proved useful for studying the Cotton-Mouton effects of magnetic fluid.[6]

In the present study, we investigted a magnetic fluid solution in which the particles at the surface of the fluid were modified by organic compounds which emit fluorescence upon irradiation by light, i.e., they are assumed to be gathered on the surface of magnetic particles.

Before examining the method for modifying the particles at the surface of the magnetic fluid, we inspected the percentage of polarized light that was absorbed by a sol of magnetic fluid. The concentration-dependence of the absorption ratio was examined using lights that were polarized parallel and perpendicular to the magnetic field. These results could provide useful information on the nature of a dilute magnetic fluid solution.

Experimental

Reagents

Magnetic fluid (type HC-50) was purchased from Taiho Industrial Co. Ltd. ; its composition was about 50 wt% magnetite, 10 wt% oleic acid (surfactant) and 40 wt% kerosene.

Derivatives of anthracene (anthracene, 1-methylanthracene, 2-methylanthracene, 9-methylanthracene, 9,10-dimethylanthracene, 9-phenylanthracene and 9.10-diphenylanthracene; Aldrich Co) were used as fluorescent dyes. Solvents such as benzene, hexane, and heptane were purchased from Nacalai Tesque.

Instruments

Figure 1 shows a schematic representation of the equipment used in this experiment. The magnet used was part of a mass spectrometer. The magnitude of the magnetic field measured by a Gaussmeter was 0.94 T. Pieces of permanent magnet (purchased from TDK) were also used, and produced a magnetic field of 0.2 T. The instruments used in this experiment are shown in Table 1. The orientation of polarization for the source light (He-Cd laser 15 mW: 325 nm) was controlled by a 1/2-wave plate. The output of the source light was chopped and synchronized with the phase of a lock-in amplifier, and then irradiated onto the surface of a sample cell through a mirror with a 45° -tilted hole (hole diameter:2 mm). The fluorescence at the front surface of the cell was reflected by the mirror (tilted at 45°) towards a monochromator. Either the vertically or horizontally polarized fluorescence from the cell was selected by a Glan-Thompson prism. A low-cut filter was used to eliminate of source laser light into the monochromator. In front of the monochromator, a quartz depolarizer was set to eliminate the

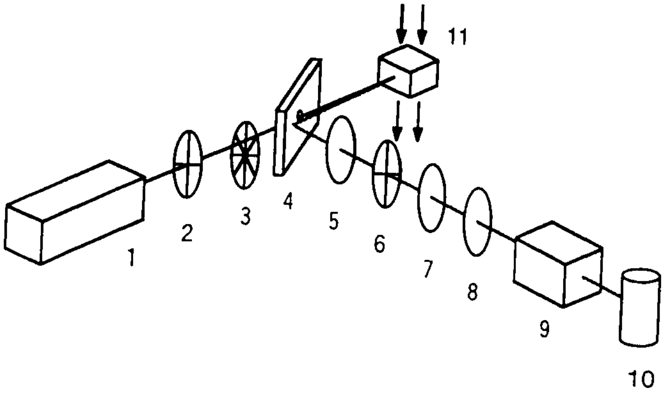

Fig. 1 Schematic representation of the present experimental system.

1:He-Cd laser (325 nm), 2:1/2 λ plate, 3:chopper, 4:45° holed mirror (hole size=2 mm), 5:convex lens, 6:Glan-Thompson prism, 7:low-cut filter (to prevent entrance of laser light), 8:depolarizer, 9:monochromator, 10:photomultiplier, 11:sample cell. The arrows in the figure show the magnetic field.

polarization characteristic of the monochromator. The output of the monochromator was fed to the lock-in amplifier via a preamplifier, and recorded by an analyzing recorder.

Procedure

Anthracene and anthracene derivatives were dissolved in solvent and mixed with a solution of diluted magnetic fluid. The mixtures of anthracene derivatives and magnetic fluid were discarded after each measurement. The fluorescence spectra of the anthracene derivatives were inspected by a fluorometer with excitation at 325 nm, and the wave-lengths that gave maximum fluorescence were confirmed. The wavelengths of the fluorescence measured were as follows:

Table 1 Instruments used in this study

Magnet	Hitachi Co. Ltd., model RMS-4
He-Cd laser	Kinmon Electric Co. Ltd., model IK 3251-RF
Light chopper	NF Electronic Instruments Co., model 5584
Photomultiplier	Hamamatsu Photonics, type R456
Power supply	Hamamatsu Photonics, model C448A
Photocell	Hamamatsu Photonics, type S1336-5BQ
Pre-amplifier	NF Electronic Instruments Co., model LI-11
Lock-in amplifier	NF Electronic Instruments Co., model 5610B
DC amplifier	Keithley Instruments Inc., model 527
Function generator	NF Electronic Instruments Co., model FG-121B
Monochromator	Japan Spectroscopic Co. Ltd., model CT-10
Glan-Laser prism	Sigma Optical Instruments Co., type GLPO-10-15AN
Glan-Thompson prism	Sigma Optical Instruments Co., type GTPC-10-25AN
Quartz depolarizer	Sigma Optical Instruments Co., type DEQ-2S
1/2λ-wave plate	Sigma Optical Instruments Co., type WPQ-2S
Lens	Sigma Optical Instruments Co., type SLB-30B-200P(f=200.5)
Low-cut filter	Toshiba Glass Co., type UV-37
45° holed mirror	Sigma Optical Instruments Co., type TFA-50C08-1-KH02-45
Fluorometer	Japan Spectroscopic Co. Ltd., model U-Best-45B
Spectrophotometer	Hitachi Co. Ltd., model 220A
Black quartz cell	GL Science Co. Ltd., type M20-B-3
Quartz cell	GL Science Co. Ltd., type S10-G-1
Gaussmeter	F.W.Bell Co., model 9200

anthracene(405 nm), 1-methylanthracene(408.5 nm), 2-methylanthracene(411 nm), 2-ethylanthracene(409 nm), 9-methylanceracene(417 nm), 9-phenylanthracene (418.5 nm), 9,10-dimethylanthracene(432 nm), and 9,10-diphenylanthracene(435 nm). Six measurements were carried out to determine the effect of a magnetic field on the fluorescence of anthracene derivatives.

Results and Discussion

Figure 2 shows the time-dependent change in fluorescence for 2-methylanthracene (1mM: M=mol dm^{-3}). upon the application of a magnetic field. When the excitation and emission (fluorescence) were polarized parallel to the magnetic field, the application of a magnetic field produced a decrease (about 5 %) in the fluorescence intensity. On the other hand, as shown in Fig. 3, when the excitation and emission(fluorescence) were polarized perpendicular to the magnetic field, application of a magnetic field producesd an increase in the fluorescence intensity(about 3 %). When perpendicular fluorescence was observed with excitation parallel to the magnetic field, no distinct change was observed. In addition, when parallel fluorescence was observed with excitation perpendicular to the magnetic field, the change in fluorescence was not as large as that between with and without magnetic field.

To study the anisotropy of the dilute magnetic fluid solution, the absorption ratio of lights that were polarized parallel and perpendicular to the magnetic field was measured, i.e., the absorption of polarized light at 514.5 nm through a suspended solution of magnetic fluid. It was assumed that the magnetic fluid particles are spherical and isotopic without a magnetic field. It was also assumed that these particles gather to produce an anisotropic assembly under a magnetic field.[7] In this case, anisotropic nature of the assembly was defined as the ratio of the absorbances of lights polarized parallel vs perpendicular to the magnetic field, i.e., the absorbance with a magnetic field are A_1' and A_2' for light polarized parallel and perpendicular to the magnetic field, respectively. The absorbance without a magnetic field is A_1 and A_2 for the respective polarized lights. In this case, the nature of anisotropic assemblies (R) can be given as:

$$R = (A_1'/A_1)/(A_2'/A_2)$$

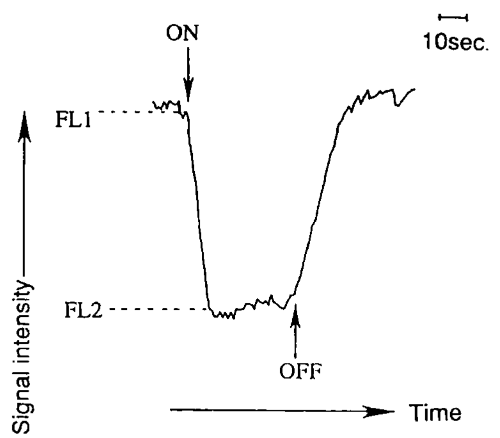

Fig. 2 Change in fluorescence intensity before and after the application of magnetic field. 2-Methylanthracene (1 mM) was measured with a magnetic fluid (0.1 mg/ml). The excitation and emission of fluorescence were measured for light polarized parallel to the magnetic field.

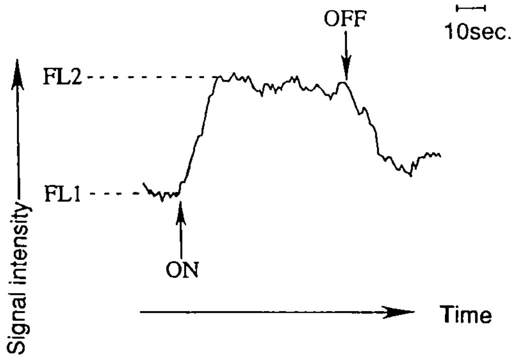

Fig. 3 Changes in the fluorescence intensity before and after the application of a magnetic field. 2-Methylanthracene (1 mM) was measured with a magnetic fluid (0.5g/ml). The excitation and emission of fluorescence were measurd for light polarized perpendicular to the magnetic field.

Figure 4 shows the value for R measured in HC-50 in benzene. There appear to be three critical ranges of R with regard to the concentration of the magnetic fluid. When the concentration of the magnetic fluid is greater than 1 mg/ml, R is constant at about 1.3. In Fig. 4, R is 1 at a concentration of less than 0.1 mg/ml, which means that a solution which contains magnetic fluid particles at a concentration of less than 0.1 mg/ml appears to be isotopic even under a magnetic field. R changes from 1.0 to 1.3 when the concentration of the magnetic fluid varies from 0.1 mg/ml to 1.0 mg/ml, and R becomes constant at about 1.3 at a concentration greater than 1.0 mg/ml.

In this study, light that was polarized parallel to the magnetic field was used to investigate the magneto-optic effect of anthracene derivatives. Figure 5 shows the relative ratio (Q) of the fluorescence intensities with and without the application of a magnetic field in benzene solution (concentrations of the anthracene derivatives were 1mM), where the concentration of the magnetic fluid was varied. In general, Q is almost constant (92 %) when the concentration of the magnetic fluid is greater than 0.25 mg/ml, except for 9,10-dimethyl anthracene, for which Q becomes a few percent smaller than with the other compounds. Among the anthracene derivatives, the Q values of 9-methyl and 2-methylanthracene also steeply decreased at a magnetic fluid concentration of less than 0.25 mg/ml. However, the Q values become the same as those for anthracene at a magnetic fluid concentration greater than 0.25 mg/ml.

A difference in Q between anthracene and 9,10-dimethylanthracene is not observed when hexane and heptane are used as solvents (Fig. 6). This variation in Q also decreased with a weaker magnetic field (0.2 T:Fig 7). However, anthracene and 9,10-dimethyl anthracene gave different Q values, just as at 0.94 T.

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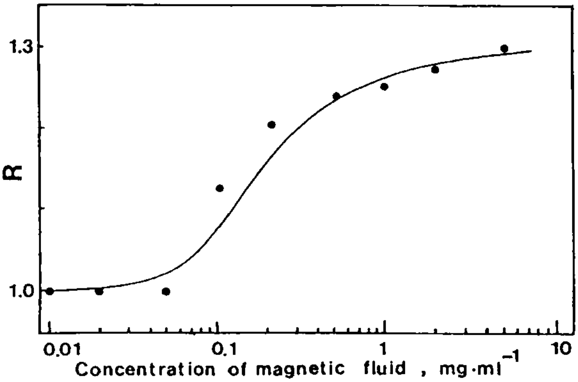

Fig. 4 Ratio(R) of the absorbance of a dilute magnetic fluid for lights polarized paralell and perpendicular to the applied magnetic field.

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A difference in Q between anthracene and 9,10-dimethylanthracene is not observed when hexane and heptane are used as solvents (Fig. 6). This variation in Q also decreased with a weaker magnetic field (0.2 T:Fig 7). However, anthracene and 9,10-dimethyl anthracene gave different Q values, just as at 0.94 T. These reflect the fact that the characteristics of the magnetic fluid sol (paramagnetic particles) are sensitive to the nature of the particles and also to the kind of the organic solvent. It should be noted that interaction between the surfactant in the magnetic fluid and the coexistent fluorescent dye is essential for

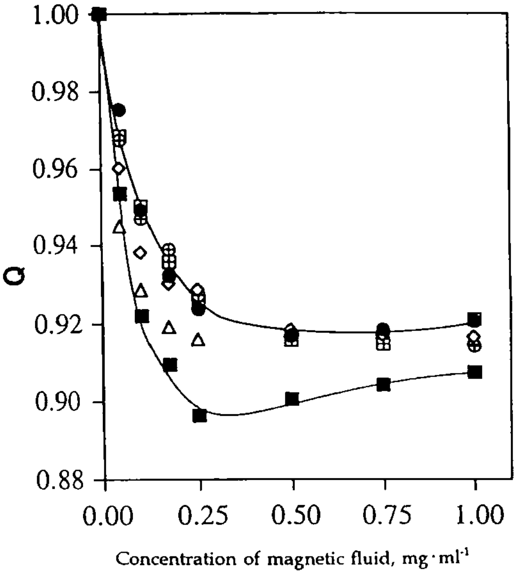

Fig. 5 Change in the fluorescence intensities of anthracene and its derivatives. The ordinate shows the ratio (Q) of the fluorescence intensity with and without the magnetic field. The concentration of the magnetic fluid is shown on the abscissa. Solvent:benzene. The excitation and emission were polarized parallel to the magnetic field.

● : anthracene, ◇ :2-methylanceracene, Δ :9-methylanthracene,

■ :9,10-dimethylanthracene, ⊞ :9,10-diphenylanthracene,

⊕ :9-phenylanthracene.

achieving the present results. When oleic acid is used as the surfactant in the magnetic fluid, it can differenciate between the anthracene derivatives with benzene solution but not with the normal aliphatic solvents. This shows that the aliphatic nature of oleic acid interacts primarily with the aliphatic solvent and not with the fluorescent dyes (anthracene derivatives). Under a weaker magnetic field, the change in fluorescence decreases while a diffrence between anthracene and

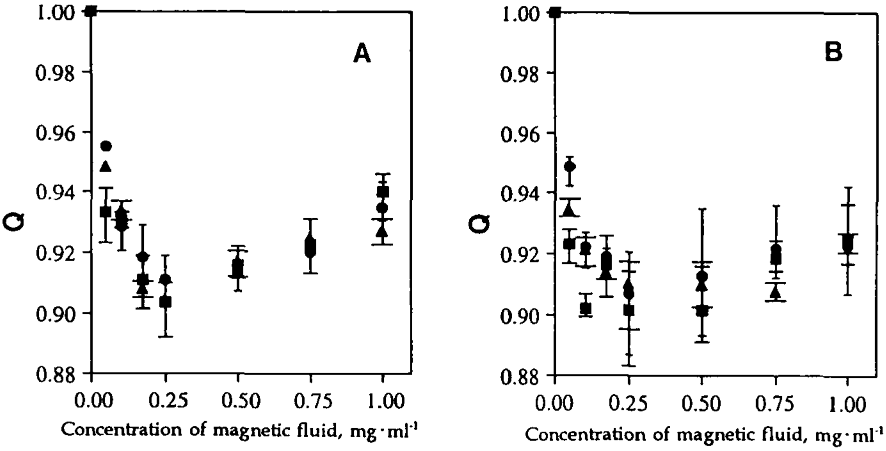

Fig. 6 The ratio(Q) of the fluorescence intensity witht and without a magnetic field. anthracene(⊢●⊣) , 9,10-dimethylanthracene(⊢■⊣), and 9-methylanthracene(⊢▲⊣), dissolved in hexane (A) and heptane (B).

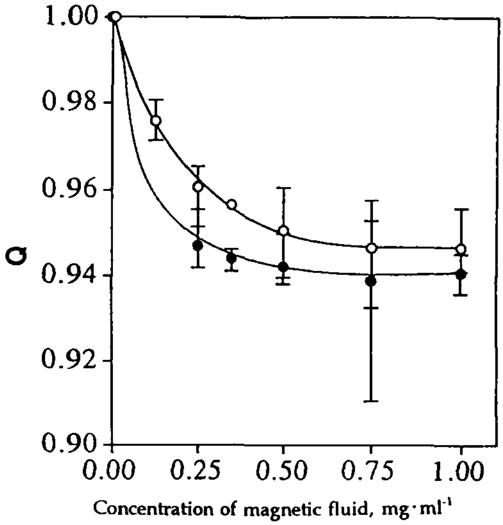

Fig. 7 Change in the fluorescence intensities of anthracene(⊢○⊣) and 9,10-dimethyl anthracene(⊢●⊣) in benzene with or without the magnetic field of 0.20 T.

9,10-dimethylanthracene appears. This also suggests the importance of interaction between the surfactant and coexistent dye in terms of molecular sensing by the magnetic fluid particles. The appearance of a magnetic field effect for the coexistent dye in a dilute magnetic fluid seems to be due to interaction between the magnetic fluid particles and the anthracene derivatives. In the present magnetic fluid, only 9,10-dimethyl anthracene showed a clearly different behavior among the anthracene derivatives. This result seems to be related to the surfactant (oleic acid) used in the present magnetic fluid(HC-50). The coexistence of a fluorescent dye may be a useful technique for inspecting the surface state of a magnetic fluid. Furthermore, the application of a magnetic field may help to provide information about molecuar sensing.

Acknowledgements

We would like to thank Mr. Koso, Aoki, Todakogyo Corp., Dr. Isao, Nakatani, and Mr. Yusuke Matsumura, Toiho Industrial Co. Ltd. This research was supported by a grant-in-aid (#08454236) from the Ministry of Education, Science, and Culture, Japan.

References

1. T. Nomizu, H. Nakashima, M. Sato, T. Tanaka, H. Kawaguchi, Anal. Sci., 12, 829 (1996).
2. S. Taketomi, Jpn. J.Appl. Phys., 22, 1137 (1983).
3. S. Taketomi, M. Ukita, M. Mizukami, H. Miyajima and S. Chikazumi, J. Phys. Soc. Jpn. 56, 3362 (1987).
4. S. Taketomi, S. Ogawa, H. Miyajima, S. Chikazumi, K. Nakao, T. Sakakibara, T. Goto and N. Miura, J. Appl. Phys. 64, 5846 (1988).

5. S. Taketomi, Kotaibutsuri, 24, 417 (1989).

6. K. Fujiwara, R. Kojyo, H. Tsubota, K. Seki, Anal. Sci., 6 207 (1990).

7. I. Nakatani, M. Hijikawa and K. Ozawa, J. Magn. Magn. Mater., 122, 10 (1993).

Date Received: February 6, 1997
Date Accepted: April 3, 1997