Articles

Fluorescence quenching of anthracene by *N*, *N*-diethylaniline in the O/W microemulsion

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Photoinduced electron-transfer system of anthracene-*N*, *N*-diethylaniline (DEA) was studied in the oil in water (O/W) microemulsions formed by SDS (sodium dodecyl sulfate), BA (benzyl alcohol) and H_2O. The time-resolved fluorescence study showed that the fluorescence quenching of the excited anthracene by DEA occurs at the interface of the O/W microemulsions. Besides as the quencher of the excited anthracene, *N*, *N*-diethylaniline could act as a cosurfactant to change the structures of the microemulsions, just as BA did. The quenching rate constants for the different structures of the system were determined.

Keywords Electron transfer processes, fluorescence quenching, anthracene, microemulsion

Introduction

Microemulsions play important roles in biology, material, the environment, and other relative fields.[1] Its ability to dissolve and compartmentalize both polar and non-polar reactants has a significant effect on chemical reactivity. In an O/W microemulsion, the non-polar reactant is dissolved in the oil droplet, with the polar reactant in the water continuum. Chemical reaction occurs when there is an encounter at the interface, or one reactant is transported across the interface. During the last decade, considering the importance in biology, chemistry and energy storage,[2,3] photoinduced electron transfer processes in various types of organized systems have been the subject of intensive research.[4-6]

In homogeneous solvents, a simple, but well understood electron-transfer system was anthracene-*N*, *N*-diethylaniline (DEA). Photoexcitation of this system leads to the formation of charge-transfer excited complexes in nonpolar media and ions in polar media.[7] However, its detailed photochemical behavior in different types of organized assemblies is not understood well by now.

Recently, our laboratory has studied the phase behavior and the structure of the SDS/BA/H_2O system, and demonstrated that, in the isotropic region connected with water corner (O/W microemulsion) on its phase diagram (L_1 region in Fig. 1), there exist three small areas composed of rod, spherical, and bicontinuous structures, respectively.[8]

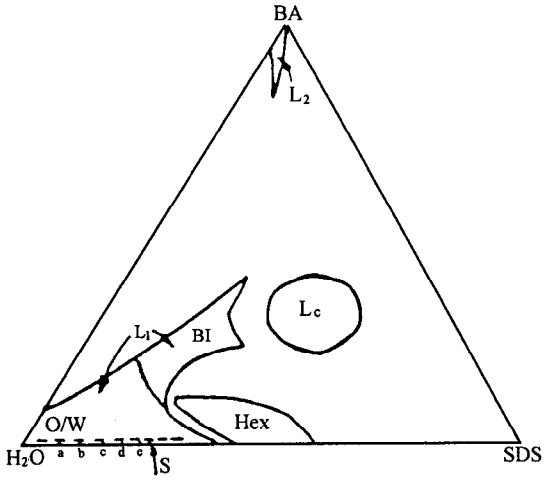

Fig. 1 Partial diagram of the SDS /BA/H_2O system. L_1-isotropic region consisting of rod (S), spherical (O/W), and bicontinuous structure (BI); L_2-W/O microemulsion; L_c-lamellar liquid crystal; Hex-hexagonal liquid crystal.

In the present paper, we will continue to examine

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the fluorescence quenching of anthracene by DEA *via* photoinduced electron transfer in the different structures of this O/W microemulsion.

Experimental

Materials

Sodium dodecyl sulfate (SDS) was obtained from Sigma (98%) and was recrystallized twice in ethanol. Benzyl alcohol (BA), anthracene and *N*, *N*-diethylaniline (DEA) were of analytical grade from Shanghai chemicals. Water used was deionized and distilled. All solutions were degassed by prolonged bubbling with nitrogen.

Fluorescence lifetime

Time-resolved fluorescence spectra of anthracene (2×10^{-6} mol/L) in the O/W microemulsions formed by SDS, BA and H_2O with and without DEA were recorded on a Horible NAES-1100 single photon counting fluorescence spectrophotometer. The fluorescence was excited and recorded at 350 nm and 400 nm, respectively, at the room temperature.

Fluorescence quenching

Steady state fluorescence spectra of anthracene (2×10^{-6} mol/L) were recorded with a Shimadzu RF-540 fluorescence spectrophotometer in this O/W microemulsion with an increasing amount of DEA at the room temperature. Anthracene was excited at 350 nm.

Determination of the diffusion coefficient

The diffusion coefficient was calculated from the cathodic peak current measured by electrochemical experiments.[9]

Electrochemical measurements were conducted in a three-electrode configuration with platinum as the working electrode, platinum plate as the auxiliary electrode and a saturated calomel electrode (SCE) as the reference electrode. After a continuous flow of nitrogen, the cyclic voltammogram for SDS solution can be obtained at platinum electrode with the swept potential.

Determination of micellar aggregation number N

The aggregation number *N* of SDS micelle was determined through the traditional stable-state fluorometry as described in reference 8. Pyrene (5×10^{-6} mol/L) was used as the probe and cetylpyridine chloride (CPC) as the quencher. *N* can be determined by measuring the total intensity of pyrene fluorescence with and without CPC.[8]

Measurement of the micro-environment of the microemulsions

Pyrene is used as the probe to determine the micro-environment of the microemulsions by observing its fluorescence fine structure.[10] The fluorescence spectrum of pyrene is formed by 5 peaks, which are marked 1 through 5 from the shortest wavelength peak. By the intensity of I/III peak ratio I_1/I_3 which is sensitive to pyrene environment, the micro-environment of the microemulsions can be measured.

Results and discussion

Life time of the excited anthracene in the O/W *microemulsion formed by* SDS, BA *and* H_2O

In the previous study,[8] we have illustrated the structure of the O/W microemulsion formed by SDS, BA and H_2O (L_1 region in Fig. 1). Measurements of the

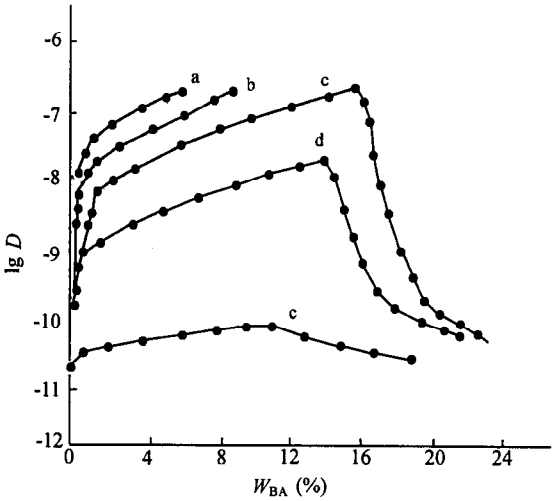

Fig. 2 Diffusion coefficient of micelle with BA concentration in the different weight ratios of SDS/H_2O. SDS/H_2O: (a) 5/95; (b) 10/90; (c) 16/84; (d) 18/82; (e) 22/78 (sample numbers are similar to Fig. 1).

diffusion coefficient (Fig. 2) show that the L_1 region

consists of three subregions, rod, spherical, and bicontinuous structures. In this section, we will study the fluorescence life time of the excited anthracene in this region with and without DEA.

Table 1 Fluorescence life time of anthracene in SDS/BA/H_2O system

SDS:H_2O	BA (%)	C_{DEA} (mol/L)	τ_1 (ns)[b]	τ_2 (ns)[b]	χ^2
2.0:98.0	1.0	0	3.50	20.5	1.05
2.0:98.0	1.0	0.0040[a]	2.17	20.5	1.00
2.0:98.0	4.0	0	3.50	18.3	1.08
16.0:84.0	1.0	0	3.73	14.0	1.31
16.0:84.0	1.0	0.028[a]	2.23	13.7	1.00
16.0:84.0	12.7	0	3.17	10.0	1.27
16.0:84.0	12.7	0.019[a]	2.50	10.1	1.13
16.0:84.0	16.5	0	3.18	13.2	1.23

[a] Concentration of DEA at the structural change point; [b] Simulated by convolution method and the error limitation is ± 10%.

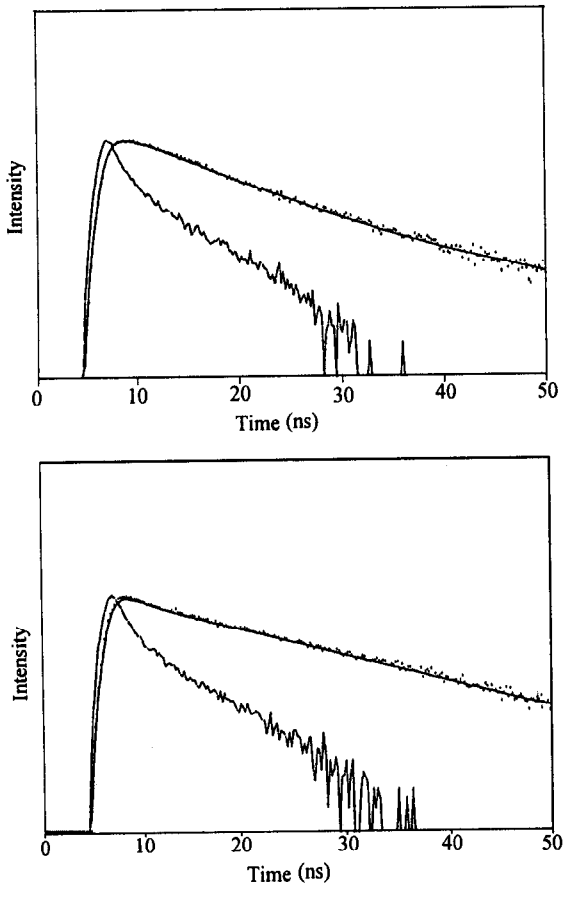

Fig. 3 Decay curve of anthracene fluorescence at SDS/H_2O = 16.0/84.0 with [DEA] = 0 (top) and 0.0058 mol/L (bottom).

At the weight ratios of SDS:H_2O being 2.0:98.0 and 16.0:84.0, no matter with or without DEA, the fluorescence decay of anthracene was double exponential, as shown in Fig. 3. From the curve, two life time, τ_1 and τ_2 (shown in Table 1) were obtained. From Table 1, we can also see that, at the presence of DEA, the fast decay (τ_1) became faster, while the slow decay (τ_2) unchanged if considering the error limitation (± 10%). In this microemulsion, it is clearly that anthracene may exist not only at the interface, but also in the oil pool. The fast decay (τ_1) corresponds to that of the excited anthracene at the interface, slow decay (τ_2) to the anthracene resided in the oil pool. However, DEA tends to reside at the interface for its association with BA or H_2O by the hydrogen bonds. Considering the fact[7] that DEA can quench the fluorescence of anthracene by single electron transfer, at the presence of DEA, only the excited anthracene existing at the interface can be quenched, which results in that τ_1 decreases while τ_2 is unchanged. Table 2 shows the effect of the concentration of DEA on the life time τ_1. When the weight ratio of SDS/H_2O is 16.0/84.0 and the content of BA is 12.7% (spherical O/W, Figs. 1 and 2), with the addition of DEA, life time τ_1 decreases firstly. But when the concentration of DEA reaches 0.019 mol/L, τ_1 is almost unchanged, and then, with the further addition of DEA, τ_1 continues to decrease. This is because that, besides as the quencher of the excited anthracene, DEA can also play the role of cosurfactant in this system, which may cause the spherical structure of the microemulsion to become bicontinuous structure at certain concentration just as BA does (see Figs. 1 and 2). When the content of BA is 16.5%, with the addition of DEA, life time τ_1 decreases continuously and there is no change point. As illustrated in Figs. 1 and 2, in this

case, the addition of cosurfactant BA can not change its bicontinuous structure, nor does DEA. The life time τ_1 and the concentration of DEA at the structural change point with BA content at SDS : H_2O being 16.0 : 84.0 and 2.0:98.0 are listed in Table 1. The detailed experiments and results on the structural change of the microemulsions caused by DEA will be discussed in the following sections.

Fluorescence quenching of the excited anthracene by N, N-diethylaniline (DEA) *in the* O/W *microemulsion*

The results in the above section clearly show that the quenching of the excited anthracene by DEA is exponential and occurs at the interface. Fig. 4 illustrates the quenching data when BA content are 1.0% and 4.0% at the weight ratio of SDS/H_2O being 2.0/98.0, respectively. In Fig. 4, I_f and I_0 are the fluorescence intensity of the excited anthracene with and without DEA, respectively. In Fig. 4a (BA = 1.0 %), two lines are formed. According to Fig. 1, when BA is 1.0%, the structure is rod, which can be changed to spherical with

Table 2 Life time τ_1 with the addition of DEA (SDS : H_2O = 16.0:84.0, BA = 12.7% and 16.5%)

SDS:H_2O	BA (%)	C_{DEA}(mol/L)	τ_1(ns)
16.0:84.0	12.7	0	3.17
16.0:84.0	12.7	0.006	2.87
16.0:84.0	12.7	0.012	2.56
16.0:84.0	12.7	0.019	2.50
16.0:84.0	12.7	0.025	2.08
16.0:84.0	16.5	0	3.18
16.0:84.0	16.5	0.006	2.91
16.0:84.0	16.5	0.012	2.66
16.0:84.0	16.5	0.019	2.40
16.0:84.0	16.5	0.025	2.15

the addition of BA. For DEA can also play the role of cosurfactant like BA, it can cause the change of the microemulsion's structure. So, the line relative to the lower concentration of DEA shows the quenching in rod structure, while the second line corresponds to the quenching in the spherical microemulsion. The change point at C_{DEA} = 0.0040 mol/L indicates the structural change, which agreed with the results described in the above section. However the plot of Fig. 4b (BA = 4.0%) is linear. According to Fig. 1, at BA = 4.0%, the structure is spherical, which can not be altered with the further addition of BA, nor does DEA. The change of the microemulsion's structure by DEA was also demonstrated both by the measurements of the aggregation number N of SDS at different concentration of DEA and by the effect of DEA concentration on the microemulsion's micro-environment.

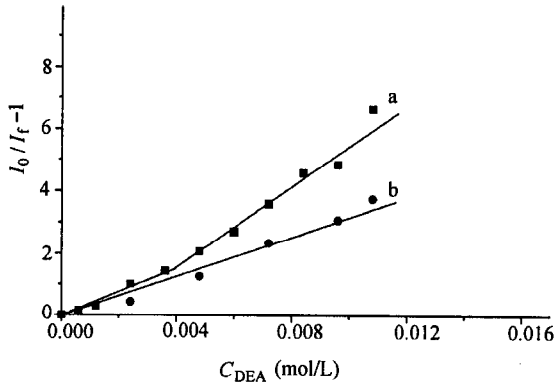

Fig. 4 Quenching of the excited anthracene (2×10^{-6} mol/L) by DEA with BA = 1.0% (a) and 4.0% (b) in SDS/H_2O = 2.0/98.0, I_f and I_0 are the fluorescence intensity of the excited anthracene with and without DEA, respectively.

Fig. 5 shows the plot of the aggregation number N *vs*. the concentration of DEA when SDS/H_2O = 2.0/98.0. If BA = 1.0% (Fig. 5a), with the addition of DEA up to 0.0040 mol/L, the aggregation number N decreases quickly. And then, a continuously increasing DEA content only results in a slow decrease of the aggregation number N. From Fig. 1, we have known that, in this case, with the addition of BA, the microemulsion's structure can change from rod to spherical. Because DEA can act as cosurfactant like BA, it is possible that the structure may change from rod to spherical at DEA = 0.0040 mol/L, which leads to the decreasing curve of SDS aggregation number N with DEA as shown in Fig. 5a. When BA content is 4.0%, with the addition of DEA, the aggregation number N decreases continuously (Fig. 5b) because the structure in this case can not be changed by further addition of DEA, which can be deduced from the little effect of the increasing BA on the structure (Fig. 1).

Fig. 6 shows the dependence of the intensity of I/III peak ratio I_1/I_3 of the fluorescence spectra of pyrene in the above system on the concentration of DEA. It has been established that the intensity of I/III peak ratio $I_1/$

I_3 of pyrene fluorescence spectrum was sensitive to its micro-environment.[10] When BA = 1.0% (Fig. 6a), the ratio I_1/I_3 decreases suddenly at [DEA] = 0.0040 mol/L, which shows that the structure may be suddenly changed. While when BA content is 4.0%, with the addition of DEA, the ratio I_1/I_3 is almost unchanged (Fig. 6b).

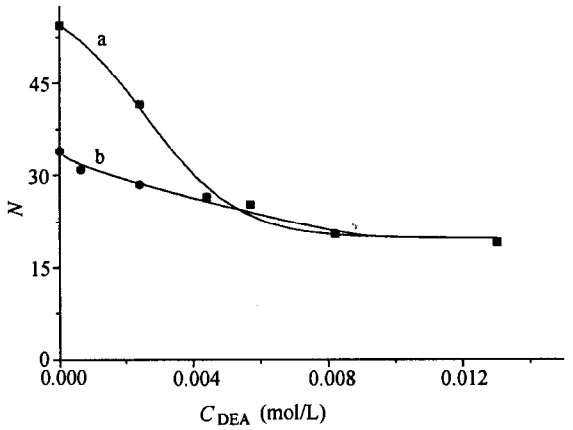

Fig. 5 Dependence of SDS aggregation number N on the concentration of DEA with BA = 1.0% (a) and 4.0% (b) in SS/H_2O = 2.0/98.0.

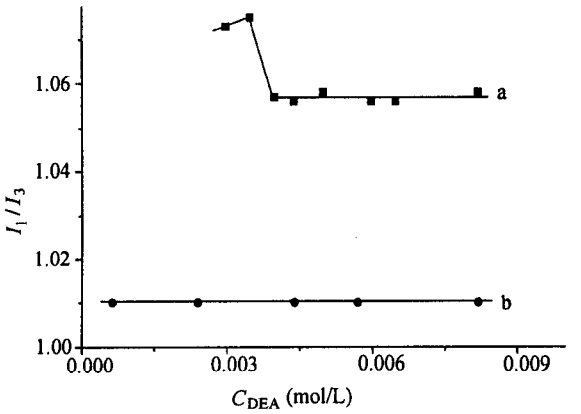

Fig. 6 Dependence of the intensity of I/III peak ratio I_1/I_3 of pyrene (5×10^{-6} mol/L) fluorescence spectra on the concentration of DEA with BA = 1.0% (a) 4.0% (b) in SDS/H_2O = 2.0/98.0.

The concentration of DEA at the structural change point of the O/W microemulsions demonstrated by the micro-environment and the aggregation number N of SDS with the different weight ratios of SDS/H_2O and BA content is consistent with the results discussed in the first section.

According to the above discussion, the quenching rate constants of anthracene by DEA can be calculated by Stern-Volmer equation, which is,

$$I_0/I_f - 1 = K[Q] \quad (1)$$

$$k_q = K/\tau_1 \quad (2)$$

where K is the quenching constant and k_q is the quenching rate constant. Before the structure change occurs, I_f and I_0 are the fluorescence intensity of the excited anthracene with and without DEA, respectively, [Q] is the concentration of DEA and τ_1 is the fluorescence lifetime of anthracene resided at the interface without DEA (Table 1). Otherwise, I_0 and I_f are the fluorescence intensity of the excited anthracene at the change point and with the further addition of DEA, respectively. [Q] is equal to the overall concentration of DEA minus the concentration of DEA at the change point, and τ_1 is the fluorescence lifetime of anthracene resided at the interface with DEA having the concentration just leading to the microemulsion's structure change (shown in Table 1). The rate constants for these photoinduced electron transfer reactions and the corresponding structures of the microemulsions were summarized in Table 3.

Fig. 7 illustrates the quenching data in the O/W microemulsion with the weight ratio of SDS/H_2O = 16.0/84.0. Fig. 7a (BA = 1.0%) and Fig. 7b (BA = 12.7%) are composed of 2 lines but Fig. 7c (BA = 16.5%) is linear. According to Figs. 1 and 2, at BA content is 1.0% and SDS/H_2O = 16.0/84.0, the structure is rod, which can be changed to spherical with the addition of cosurfactant. So, in Fig. 7a, the line with the lower concentration of DEA shows the quenching data in the rod structure, while the second line corresponding to the reaction occurring in the spherical microemulsion. The change point at [DEA] = 0.028 mol/L represents the point of the structural change. When BA content is 12.7%, the structure is spherical, which can be changed to bicontinuous with the addition of cosurfactant. So, in Fig. 7b, the line with the lower concentration of DEA shows the quenching data in the spherical microemulsion, while the second line corresponding to the reaction occurring in the bicontinuous microemulsion. The change point at [DEA] = 0.019 mol/L represents the point of the structural change. When BA = 16.5%, the microemulsion's structure is

bicontinuous, which can not be altered with the further addition of cosurfactant just as shown in Figs. 1 and 2. All of the concentration of DEA at the change point of the above plots are consistent with the results shown in Table 1. Furthermore, the structural change caused by DEA was also proved by the intensity of I/III peak ratio I_1/I_3 of pyrene fluorescence spectra at the presence of DEA (Fig. 8). According to Fig. 7 and Eqs. (1) and (2), we can calculate the rate constants for the fluorescence quenching of the excited anthracene by DEA. All these quenching data are listed in Table 3.

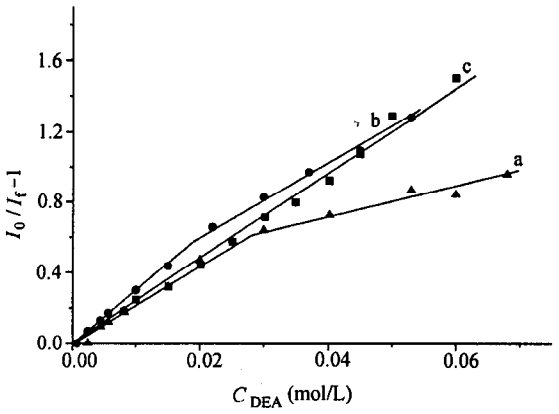

Fig. 7 Quenching of the excited anthracene (2×10^{-6} mol/L) by DEA with BA = 1.0% (a), 12.7% (b) and 16.5% (c) in SDS/H_2O = 16.0/84.0, I_f and I_0 are the fluorescence intensity of excited anthracene with and without DEA, respectively.

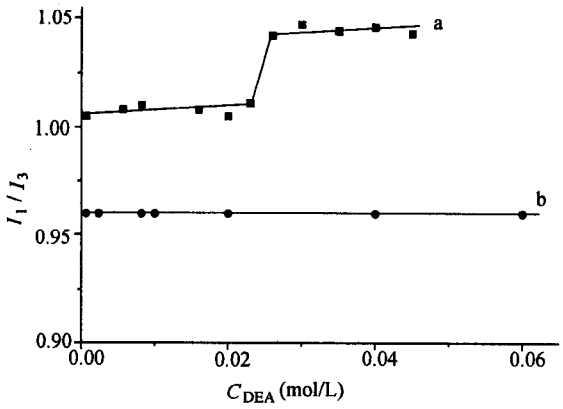

Fig. 8 Dependence of the intensity of I/III peak ratio I_1/I_3 of pyrene (5×10^{-6} mol/L) fluorescence spectra on the concentration of DEA with BA = 12.7% (a) and 16.5% (b) in SDS/H_2O = 16.0/84.0.

From Table 3, it can be found that, the rate constant k_q is largely dependent on the content of SDS. From Fig. 6 and Fig. 8, we can see that, to the similar structure, the micro-environment polarity of SDS/H_2O/BA system becomes more hydrophobic when the weight ratio of SDS/H_2O varies from 2.0/98.0 to 16.0/84.0, *i.e.*, the intensity of I/III peak ratio I_1/I_3 becomes smaller. So, the lower concentration of SDS leads to the faster quenching rate constant in L_1 region just as shown in Table 3.

Table 3 Rate constants for the fluorescence quenching of the excited anthracene by DEA in the O/W microemulsion formed by SDS-H_2O-BA and the concentration range of DEA for a microemulsion's structure

SDS:H_2O	BA (%)	k_q (L/mol s^{-1}) $\times 10^{-9}$	C_{DEA} (mol/L)	Structure
2.0:98.0	1.0	123.15	0—0.0040	rod
2.0:98.0	1.0	137.29	0.0040—0.016	spherical
2.0:98.0	4.0	93.21	0—0.016	spherical
16.0:84.0	1.0	5.42	0—0.028	rod
16.0:84.0	1.0	2.21	0.028—0.080	spherical
16.0:84.0	12.7	9.24	0—0.019	spherical
16.0:84.0	12.7	4.22	0.019—0.080	bicontinuous
16.0:84.0	16.5	7.67	0—0.080	bicontinuous

Diffusion coefficient of the O/W microemulsion at the presence of DEA

The structural change of the O/W microemulsion was also demonstrated by the diffusion coefficient of SDS micelle determined by the cyclic voltammogram.

Fig. 9 shows that the cathodic peak potential i_p is independent of the sweep rate. From Fig. 9, we can also see that cathodic peak potential i_p is proportional to the square root of the potential sweep rate. Thus, the electrochemical progress of SDS micelle solution is reversible.

For a reversible wave, the relationship of the peak current i_p(amperes) with potential rate υ (V/s), solu-

tion concentration C_0 (mol/L), the area of electrode A (cm^2) and the partical diffusion coefficient D_0 (cm^2/s) is as followed,[9]

$$i_p = 2.69 \times 10^5 \, n^{3/2} \, C_0 D_0^{1/2} \, \upsilon^{1/2} \, A \qquad (3)$$

The number of electrons per SDS molecule oxidized or reduced, n, can be obtained from the relation of the peak potentials E_p to the half-peak potentials $E_{p/2}$.[9] For the SDS reaction at the platinum electrode, $n \approx 1$.[11]

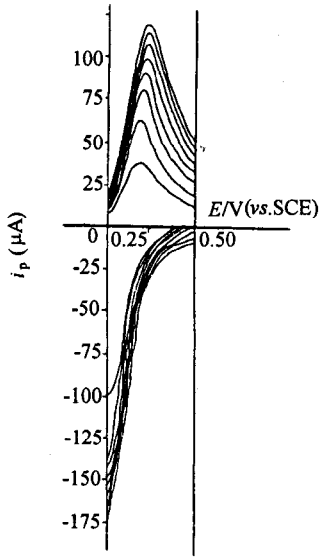

Fig. 9 Cyclic voltammogram at different potential sweep rates for the SDS/BA/H_2O/DEA system.

Fig. 10 shows that the diffusion coefficient of SDS varies with the DEA content at SDS/H_2O = 2.0/98.0. When BA content is 1.0% (curve a in Fig. 10), there is one sudden change when the concentration of DEA is 0.0040 mol/L, which means the structural change of the microemulsion. This is because that, besides as the quencher of the excited anthracene, DEA can also play the role of cosurfactant in this system, which may cause the rod structure of the microemulsion to become spherical structure at certain concentration just as BA does (see Fig. 1). However, when BA content is 4.0% (curve b in Fig. 10), there is no change. According to Fig. 1, at BA = 4.0%, the structure is spherical, which can not be altered with the further addition of BA, nor does DEA.

All of the conclusions deduced from the diffusion coefficient of SDS with the DEA content are consistent with the results discussed in the above sections.

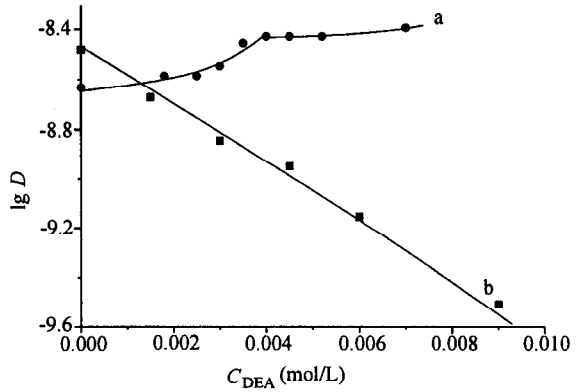

Fig. 10 Diffusion coefficient of micelle with DEA concentration at BA = 1.0% (a) and 4.0% (b) in SDS/H_2O = 2.0/98.0.

Conclusions

In this paper, we have studied the fluorescence quenching of anthracene by N,N-diethylaniline (DEA) in the oil in water (O/W) microemulsions formed by SDS (sodium dodecyl sulfate), BA (benzyl alcohol) and H_2O. The fluorescence quenching occurs at the interface of the O/W microemulsions and the quenching rate constant k_q is largely dependent on the content of SDS. Besides as the quencher of the excited anthracene, N,N-diethylaniline could act as a cosurfactant to change the structures of the microemulsions, just as BA did.

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