Colloid Polym Sci 274:747–753 (1996)

ORIGINAL CONTRIBUTION

J.B. Huang
G.-X. Zhao

Fluorescence probes study on the mixed cationic–anionic surfactant solutions

Received: 11 August 1995
Accepted: 27 December 1995

Dr. J.B. Huang (✉) · G.-X. Zhao
Institute of Physical Chemistry
Peking University
Beijing 100871, PR China

Abstract Pyrene and *p-N, N*-dimethylaminostyrylphenylmalononitrile are used as the fluorescence probes to study the micro environment and observe the excimer formation of pyrene in sodium alkylcarboxylate and alkyltrimethyl ammonium bromide mixed solutions. The micro polarity, micro-dielectric constants and micro viscosity of the self-organized assemblies in the mixed cationic-anionic surfactant solution were compared before and after sonication, which may form different organized assemblies (micelle or vesicle). The micelle and vesicles have almost the same polarity for the probing molecules whereas the micro-viscosity differs. The variation of fluorescence quenching curves also shows the different effect of the change of assembly forms (micelles to vesicles). Thus some novel physico-chemical properties about the micro environment of the cationic–anionic surfactant assemblies were found from this report.

Key words Cationic–anionic surfactant – fluorescence probe – micelle – vesicle

Introduction

With the development of photo physics and photo chemistry research, the fluorescence emission probes as a tool for investigating the micro-heterogeneous systems, such as organized assemblies, supra-molecular host-guest systems and adsorbed molecules on reactive and non-reactive surface, have been widely used because of their simplicity, wide scope and extreme sensitivity at very low probe concentrations. The fluorescence probe studies of surfactant solutions have been made rather extensively (as reviewed in ref. [1]). However, most research was usually concentrated on single surfactant solutions (cationic or anionic surfactant solutions), and the spectrofluorimetric investigation of aqueous mixture of the cationic–anionic surfactants is very scarce, mainly because of the limit of the solubility of cationic–anionic surfactant mixture. Previous reports [2, 3] have revealed spontaneous vesicle formation from the micellar solution of 1:1 C_nCOONa ($C_nH_{2n+1}COONa$)-CmNMBr($C_mH_{2m+1}N(CH_3)_3Br$) or that by ultra-sonication. In the present paper, we report an investigation using two kinds of fluorescence probes (Pyrene and *p,N,N*-dimethylaminostyrylphenylmalononitrile) to measure the micro environment in these kinds of cationic–anionic surfactant solutions. Some novel results here are from the luminescence probe method to study the micro-polarity, micro-dielectric constants and micro viscosity of the self-organized assemblies in the mixed cationic–anionic surfactant solutions before and after sonication, and fluorescence quenching curves and fluorescence lifetimes in different forms of self-organized assemblies.

Colloid & Polymer Science, Vol. 274, No. 8 (1996)

Experimental

Materials

Sodium alkylcarboxylate (CnCOONa $n = 9, 11$) was prepared from the neutralization of the corresponding carboxylic acid (CnCOOH) and NaOH at equimolar ratio in ethanol, then the solvent was removed and CnCOONa was vacuum dried. C_9COOH was double distilled and $C_{11}COOH$ was recrystallized five times in ethanol-water mixture (m.p. 43–44 °C), Quaternary ammonium bromide was synthesized from *n*-alkyl bromide and tri-methyl amine. Alkyltrimethyl ammonium bromide (C_mNMBr $m = 8, 10$) was recrystallized five times in ethanol-acetone mixture [2]. The purities of all the surfactants were examined by drop volume method [4] and the lowest point was not found on the curves of the surface tension versus logarithm of the surfactant concentration. Pyrene was recrystallized two times before use. *p-N,N*-dimethylaminostyrylphenylmalononitrile is the product of Fluka, A.R. Grade. Water was deionized water treated with $KMnO_4$ and distilled. Other reagents and solvents were products of Beijing Chemical Co., A.R. Grade.

Methods

Fluorescence measurements were recorded on Hitachi MPF-4 spectrofluorimeter. The fluorescence lifetimes were determined by Horiba NAES 1100 time-resolved spectrofluorimeter. All the fluorescence measurement was done at room temperature (~20 °C) except for viscosity measurement (at 20 ± 0.01 °C).

For the research of polarity in solution, pyrene is used as the fluorescence probe (excitation wavelength is 337 nm, concentration is 1.53×10^{-5} mol·dm^{-3}). The excimer formation of pyrene in cationic-anionic systems is also observed at 470 nm in fluorescence emission spectrum (pyrene concentration is 4.0×10^{-6} mol·dm^{-3}). The ratio of Ie/Im (Ie: at 470 nm, the peak of excimer, Im: at 392 nm, the peak of the fifth monomer peak) in the systems is used to study the pyrene excimer formation *N,N*-dimethylaminostyrylphenylmalononitrile was used as the fluorescence probe (the concentration is 2.8×10^{-5} mol·dm^{-3}, excitation wavelength is 485 nm) for the micro dielectric constants and micro viscosities measurement.

The information of fluorescence quenching was studied by using pyrene as probe and *p-N,N*-dimethylaminotolune as the quenching agent, and I_Q and I_0 are the fluorescence intensities (at $\lambda = 392$ nm) for the solution with and without the quencher, [Q] is the quencher concentration. The fluorescence lifetimes in the systems are measured by the use of the Horibra NAES1100 time-resolved fluorimeter at different quencher concentration.

The mixed surfactant vesicles were prepared by simply mixing the cationic and anionic surfactant solution at room temperature (~25 °C) or by sonicating the mixed surfactant solution for 0.5 h at 50 °C (Water-bathed Sonicator: Haitung CQ-250). The pH values of the mixed surfactant solutions were controlled at 9.2 by $Na_2B_4O_7 \cdot 10H_2O$ (~0.01 mol·dm^{-3}).

Results and discussion

The micro polarity of surfactant solutions

At room temperature, the fluorescence emission spectrum of pyrene in solution, shows five vibronic peaks. The ratio of the intensities of the first and third vibronic peaks, I_1/I_3 (I_1 at 372.6 nm, I_3 at 383.6 nm) is dependent largely on the solvent polarity [5–6], and usually it can reflect the polarity of the micro environment in which pyrene is. The micro polarity data for various surfactant solutions are listed in Table 1. The values of I_1/I_3 are 0.58, 1.14, 1.38, and 1.73 for cyclohexane, ethanol, acetic acid and water, respectively. The curves of $I_1/I_3 \sim \lg c$ (c: surfactant concentration) are shown in Fig. 1.

From Table 1, we can see that the polarity of a surfactant solution – a bit far before critical micellar concentration (CMC) – is very large, near that of water. However, with the increase of the surfactant concentration, the I_1/I_3 values of surfactant systems go down and then stay at

Table 1 Polarity of surfactant solutions (~20 °C)

Surfactant system	Concentration C/mol·dm^{-3}	CMC[a] mol·dm^{-3}	I_1/I_3
C_9COONa	5.2×10^{-3}		1.70
pH = 9.2)	5.2×10^{-2}		1.60
	0.14	0.22	1.45
	0.20		1.35
	0.25–0.30		1.11
$C_{10}NMBr$	5.2×10^{-4}		1.60
	5.2×10^{-3}	6.5×10^{-2}	1.55
	6.0×10^{-2}		1.46
	0.13–0.90		1.40
C_9COONa–	1.0×10^{-4}		1.71
$C_{10}NMBr$	1.6×10^{-3}		1.58
(pH = 9.2)	7.9×10^{-3}	9.8×10^{-3}	1.45
	6.0×10^{-2}		1.37
	$1.9–5.0 \times 10^{-2}$		1.22[b]

[a] Determined by the surface tension method [2].
[b] The same value is obtained for the solution after sonication.

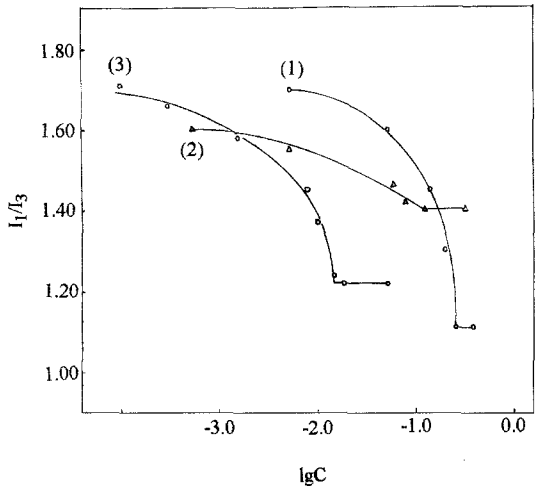

Fig. 1 Micro polarity in surfactant solutions 1) C_9COONa system; 2) $C_{10}NMBr$ system; 3) 1:1 C_9COONa-$C_{10}NMBr$ mixed system

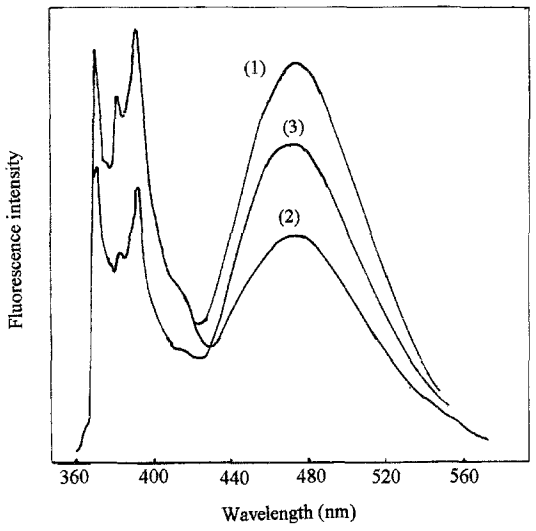

Fig. 2 Exicimer formation of pyrene in 1) 1:1 mixed C_9COONa-$C_{10}NMBr$ system (0.015 mol·dm^{-3}); 2) 1:1 mixed $C_{11}COONa$-C_8NMBr system (0.011 mol·dm^{-3}); 3) octanol solution (0.0038 mol·dm^{-3})

a final constant value. This may be because the hydrocarbon (HC) chains of surfactant molecules will aggregate in solution to form the hydrophobic micro environment in which the hydrophobic probe (pyrene) tends to locate. With the increase of surfactant concentration, more pyrene molecules are able to be solubilized in such hydrophobic micro environment. Therefore, the micro polarity of surfactant solution gradually goes down until all the pyrene molecules are surrounded by the HC chains of surfactant molecules. The final I_1/I_3 value (1.22) of 1:1 mixed C_9COONa-$C_{10}NMBr$ system is between that of C_9COONa system (1.11) and $C_{10}NMBr$ system (1.44). It is noted that all the final I_1/I_3 values in these systems-reflecting the information at the micro environment of the micelles in which pyrene locate-are smaller than that in water and larger than that in alkane, near that of ethanol or acetic acid; therefore, we can conclude that the fluorescence probe pyrene is not solubilized in the micelle center (in which polarity is near that of alkane), but in the palisade layer of micelle. It is also noteworthy that the micro-polarity of 1:1 C_9COONa-$C_{10}NMBr$ solution before sonication is the same as that after sonication, meaning that micelles and vesicles have the same micro-polarity for the probing molecules.

The fluorescence emission spectra of pyrene excimer formation in 1:1 mixed C_9COONa-$C_{10}NMBr$ and $C_{11}COONa$-C_8NMBr systems and the influences of surfactant concentration to *Ie/Im* are shown in Figs. 2 and 3. From Fig. 3, we can see the *Ie/Im* values in cationic-anionic systems go up and then down, and have a maximum value with the increase of total surfactant concentration. In some reports [7, 8] about the dye excimer formation in anionic systems, the reason for the maximum value of

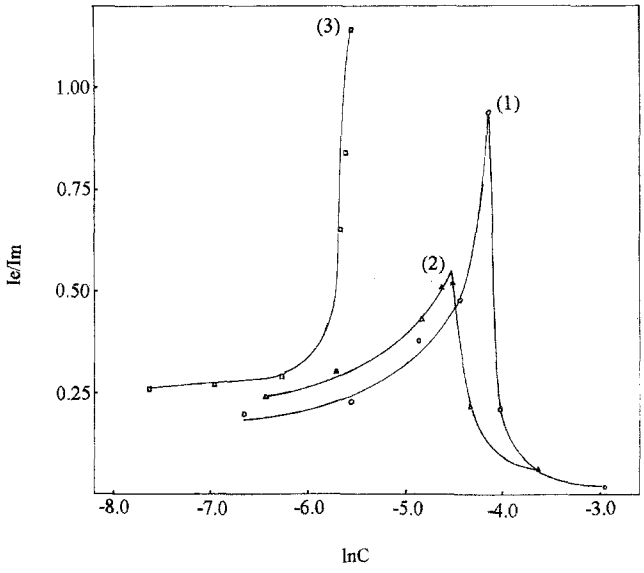

Fig. 3 The variation of *Ie/Im* in 1) C_9COONa-$C_{19}NMBr$ system; 2) $C_{11}COONa$-C_8NMBr system; 3) octanol solution

Ie/Im was thought to be the re-distribution of probe molecules, which was caused by pre-micelle or micelle. In this work, we think that the pyrene excimer formation in cationic-anionic surfactant systems was mainly caused by the hydrophobic micro environment formed by aggregation of surfactant long HC chains. Because of the hydrophobic effect, the long hydrophobic HC chains of surfactant molecules would aggregate and form the hydrophobic micro environment in aqueous solution. It

Colloid & Polymer Science, Vol. 274, No. 8 (1996)

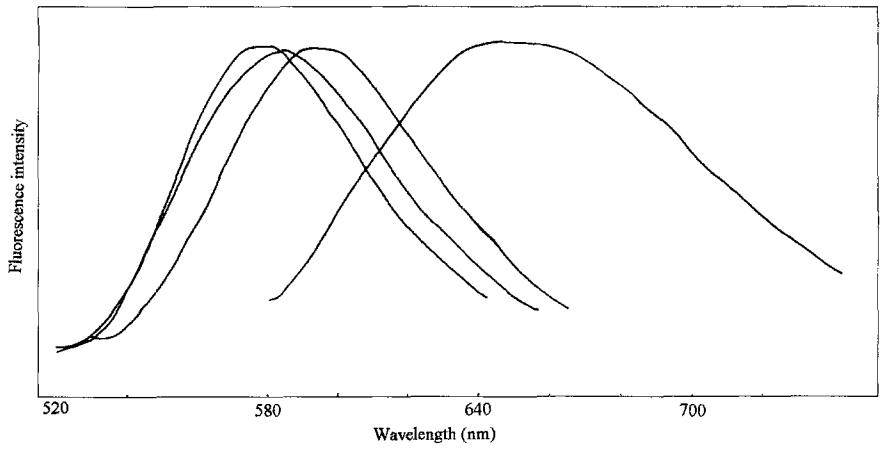

Fig. 4 The shifts of λ_{max} with the polarity of solvents (from left to right, the solvents are: chloroform, ethyl acetate, isopropanol, water)

was shown from the above results that pyrene molecules tended to be solubilized in the hydrophobic micro environment of the aggregated surfactant molecules, meaning that the concentration of pyrene would be higher in this micro environment and the excimer of pyrene may be able to form, then multiply with the increase of surfactant concentration C. If $C >$ CMC, increasingly more pyrene molecules would be solubilized in the cationic–anionic micelles. Because the pyrene concentration is very small, it is rare to have two pyrene molecules in a micelle, and the chance of pyrene excimer formation in cationic-anionic micelles is near zero, thus Ie/Im value goes down with increasing C. With the increase of the *n*-octanol concentration (no obvious changes in the viscosity of the solution), the pyrene excimer was also observed in the mixture of *n*-octanol with water (see Figs. 2, 3) and this result gives enough support to our conclusion that the excimer in these surfactant systems in mainly caused by the hydrophobic micro environment formed by aggregation of long HC chains, because there is no pre-micelle and micelle in *n*-octanol solution.

The micro-dielectric constants and viscosity of organized assembly in surfactant solutions

The fluorescence emission spectrum was studied while *p*-*N*,*N*-dimethylaminostyrylphenylmalononitrile was used as the probe [9]. The wavelength at the maximum fluorescence intensity λ_{max} and the maximum intensity (I_{max}) in the fluorescence emission spectrum will be influenced by the dielectric constants (ε) (see Fig. 4) and viscosity (η) of solvents, respectively. The $\lambda_{max} \sim \varepsilon$, $\lg I_{max} \sim \lg\eta$ curves and some data are shown in Figs. 5 and 6 and Tables 2 and 3. From Figs. 5 and 6 (i.e., the working curve), the micro viscosity dielectric constants of surfactant systems are measured by the same method. The results are listed in Tables 4 and 5. It was found that the micro viscosity of surfactant systems could be significantly changed in micelle formation. The micro viscosity after CMC is larger than that before CMC (in C_9COONa system) and almost the same while $C >$ CMC (in $C_{10}NMBr$ system), indicating that the micro-viscosity of the micelle in which the probe molecules locate is larger than that of the solution. The micro-dielectric constants in the cationic–anionic surfactant systems are smaller than that in the single ionic surfactant systems, which may be because the charges are almost neutralized in 1 : 1 mixed cationic-anionic surfactant micelles. The fact that ε in the 1 : 1 C_9COONa-$C_{10}NMBr$ solution before sonication is the same as that after sonication supports the conclusion given earlier that there is the same micro-polarity in the micelles and vesicles for this system.

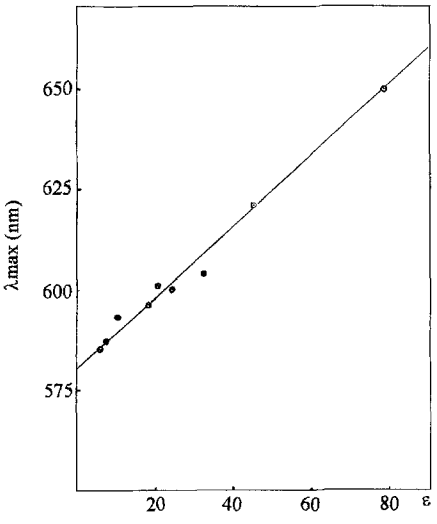

Fig. 5 The relation of $\lambda_{max} \sim \eta$

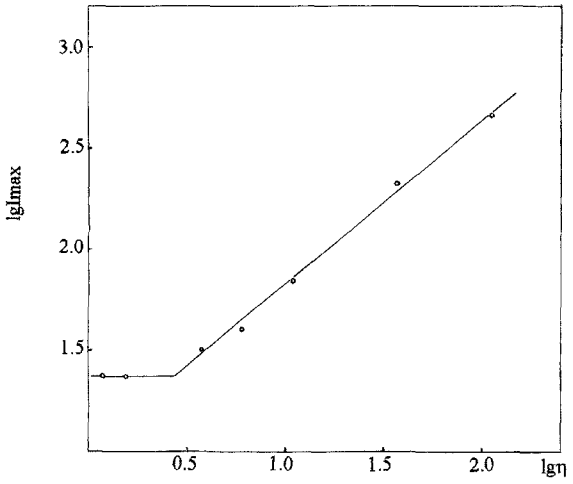

Fig. 6 The relation of $\lg I_{max} \sim \lg\eta$

Table 2 The relation of λ_{max} with ε in solvents (~20 °C)

Solvents	λ_{max}	ε [10]
acetyl acetate	585	6.0
tetrahydrofuran	587	7.6
1,2-dicholoethane	593	10.4
iso-propanol	596	18.3
acetone	601	20.9
ethanol	600	24.3
methanol	604	32.6
DMSO	621	45.0
water	650	78.3

Table 3 The relation of $\lg I_{max}$ with $\lg\eta$ in aqueous glycerol solutions (20 ± 0.01 °C)

$\lg I_{max}$	$\eta/10^{-3}$ kg·s^{-1}·m^{-1}	$\lg\eta$ [11]
1.371	1.153	0.0618
1.371	1.542	0.188
1.502	3.750	0.574
1.602	6.050	0.781
1.841	10.96	1.039
2.332	36.46	1.561
2.672	112.9	2.053

Table 5 shows some data of the micro viscosity in the two mixed surfactant systems: 1) for C_9COONa-$C_{10}NMBr$ (0.052 mol·dm^{-3}) system, 2) for $C_{11}COONa$-C_8NMBr (0.083 mol·dm^{-3}) system and one typical surfactant – sodium dodycylsulfate (SDS) solution (0.039 mol·dm^{-3}) 3), before and after sonication. The micro-viscosity (η) for solution 1) after sonication is significantly larger than that without sonication, whereas for the solutions 2) and 3), η is about the same whether they are sonicated or not. In the

Table 4 Micro dielectric constants in surfactant systems (~20 °C)

Systems	C/mol·dm^{-3}	λ_{max}	ε
$C_{10}NMBr$	0.30	608	32.5
C_9COONa[a]	0.30	608	32.5
C_9COONa-$C_{10}NMBr$[a]	5.2×10^{-2}	600	22.5[b]
C_9COONa-$C_{10}NMBr$[a]	8.3×10^{-2}	600	22.5[b]
SDS	3.9×10^{-2}	605	28.2[c]

[a] pH = 9.2, mixing ratio is 1:1 in mixed systems.
[b] The same value is obtained for the solution after sonication.
[c] The values in refs. [11–14] are between 16–49.

Table 5 Micro viscosities in surfactant systems (20 ± 0.01 °C)

Surfactant systems	Concentration C/mol·dm^{-3}	$\eta \times 10^{-3}$/kg·s^{-1}·m^{-1} NS	S[b]
C_9COONa-$C_{10}NMBr$[a]	5.2×10^{-2}	46.8	60.3
C_9COONa-$C_{10}NMBr$[a]	8.3×10^{-2}	55.2	55.2
SDS	3.9×10^{-2}	26.3[c]	26.9
$C_{10}NMBr$	0.15	23.0	
	0.30	24.0	
C_9COONa[a]	0.20	2.80	
	0.25	12.0	

[a] pH = 9.2, mixing ratio is 1:1 in mixed systems.
[b] s = sonication; NS = no sonication.
[c] The values in refs. [11, 15–16] are between 19–31.

solutions 2) and 3), whether before or after sonication, the surfactant assemblies are in the form of vesicles (mainly) and micelles, respectively. Therefore, the micro viscosities are of the same value before and after sonication. In the solution 1), only the micelles exist before sonication, and the vesicles form after sonication [2]. Then the different micro viscosities before and after sonication just demonstrate the different forms of surfactant assemblies – the vesicles would have a closer packing of surfactant molecules and hence a larger value than in the case of the micelles. It was also found that the micro viscosity of the mixed surfactant assembly is much larger than that of the single surfactant micelles. Obviously, this is due to the fact that the packing of the mixed cationic-anionic surfactant molecules in the micelles (long rod-like [17]) and vesicles are more compact than that of the single surfactant ones in the micelles (usually spherical).

The influences of organized assemblies on the fluorescence quenching and fluorescence lifetime

The fluorescence quenching was studied by using pyrene as probe and *p-N,N*-dimethylaminotolune as the quenching agent, The fluorescence quenching curves are shown in Fig. 7. For $C_{11}COONa$-C_8NMBr (0.083 mol·dm^{-3})

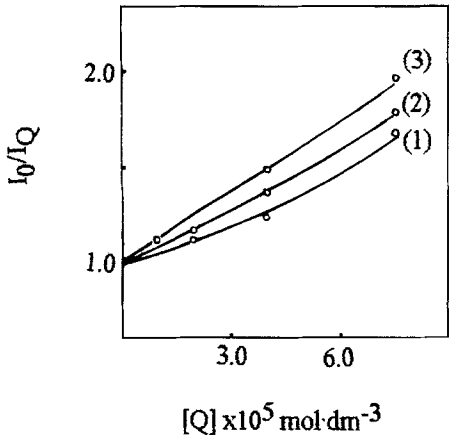

Fig. 7 Fluorescence quenching curves: 1) and 3) C_9COONa-$C_{10}NMBr$ system (0.052 mol·dm^{-3}) before or after sonication, respectively; 2) $C_{11}COONa$-C_8NMBr system (0.083 mol·dm^{-3})

system (2), the quenching curves are the same (in one curve) before and after sonication, showing that no change of the assembly occurs. However, for C_9COONa-$C_{10}NMBr$ (0.052 mol·dm^{-3}) system, there are two fluorescence quenching curves (1) and (3) – without or with sonication, respectively, indicating the change of the assembly form from micelles to vesicles before and after sonication – which is in accord with the results from the above-mentioned micro viscosity and electron-microscopy studies [2].

In the heterogeneous system, the fluorescence quenching would obey the Stern–Volmer equation:

$$I_0/I_Q = 1 + Kq/K_0[Q] \quad (1)$$

(Kq, K_0 is the rate constant of the reaction with or without quencher, respectively). However, if there are micelles in the solutions, the dynamic quenching and static quenching are both in the fluorescence quenching process. Thus the quenching curve is not a straight line [18–19]. But, for the systems containing vesicles the fluorescence quenching will obey the Stern-Volmer equation [20]. From Fig. 7, we can see that the quenching curve of C_9COONa-$C_{10}NMBr$ (0.052 mol·dm^{-3}) system after sonication (mainly containing the cationic–anionic surfactant vesicles) is nearly a straight line.

Table 6 Fluorescence lifetimes (T) in C_9COONa-$C_{10}NMBr$[a] system

Q/mol·dm^{-3}	T^{bs}	T^{as}
0	1.54×10^{-2} ns	1.28×10^{-2} ns
1.0×10^{-5}	1.34×10^{-2} ns	1.16×10^{-2} ns
3.0×10^{-5}	1.16×10^{-2} ns	1.05×10^{-2} ns

Q: Quencher concentration.
T^{bs}: Fluorescence lifetime before sonication.
T^{as}: Fluorescence lifetime after sonication.

The fluorescence lifetimes in 1:1 mixed C_9COONa-$C_{10}NMBr$ (0.052 mol·dm^{-3}) mixed systems are measured at different quencher concentration and the results are listed in Table 6. It was found that the fluorescence lifetimes are different before and after the sonication. The systems mainly containing micelles have longer lifetimes of the fluorescence probe than that of the system mainly containing vesicles, indicating that two forms of organized assemblies, vesicles and micelles, have different influences on fluorescence lifetime.

Conclusion

Micro-environment in surfactant systems was measured by using the fluorescence probe. Micro polarity in surfactant solutions will decrease with surfactant concentrations C, and increase at $C >$ CMC due to the effect of the hydrophobic micro-environment formed by HC chains in surfactant molecules, in which pyrene excimer can form. The micro-viscosity in vesicles formed in cationic–anionic surfactant systems is larger than that in long rod-like micelles because the mixed surfactant molecule is more compact in the vesicles. On the other hand, the micro dielectric constants and the micro polarity are the same in vesicles and micelles for surfactant systems. The different forms of organized assemblies (vesicles or micelle) can also have obvious influences on the fluorescence quenching and fluorescence lifetime. Thus the physico–chemical properties in the micro environment of cationic–anionic assemblies were understood further.

Acknowledgment The authors wish to thank Professor Wu S.K. and Professor Jiang Y.C. for their generous support of this work.

References

1. Zana R (eds) (1987) Surfactants in solutions: New methods of investigation. Marcel Dekker Inc, New York, Ch 5
2. Huang J-B, Zhao G-X (1995) Colloid polymer Sci 273:156
3. Zhao G-X, Huang J-B (1992) Acta Phsico-chimica Sinica 8:583
4. Zhu B-Y, Zhao G-X (1981) HuaXue TongBao, 6:341
5. Thomas JK (1980) Chem Rev 80:283
6. Kalyanasundaram KD (1977) J Phys Chem 81:2176
7. Kusumoto Y, Shizuka M, Sataka I (1986) Chem Lett 529

8. Sato H, Kawasaki M, Kasatani K (1981) J Photochem 243
9. Wang P-F, Wu S-K (1993) Photographic Sci and Photochem 11:28
10. Gordan AJ, Ford RA (1972) The Chemist's Companion. Wiley, New York
11. John AD (eds) Lang's Handbook of Chemistry. McGraw-Hill book Company, 11th
12. Law KY (1981) Photochem Photobiol 33:799
13. Zana R (1986) J Chem Soc Faraday Trans I 82:109
14. Zana R (1983) J Colloid Interface Sci 96:288
15. Mukerjee P, Cardinal JR (1978) J Phys Chem 82:1620
16. Zachariasse KA (1978) Chem Phys Lett 57:429
17. Yu Z-J, Zhao G-X (1989) J Colloid Interface Sci 130:421
18. Timpe H, Turro NJ (1983) Chem Phys Lett 99:275
19. Henglein A, Scheerer R (1978) Ber Bunsenges Phys Chem 82:1107
20. Miller DD, Magid LJ, Evans DF, J Phys Chem 94:5921