

## Energy-transfer Process Accelerated by the Formation of Electrostatically Stabilized Aggregate (ESAg)

Xi Kui JIANG\*, Jian She WANG, Ji Liang SHI

Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences,  
Shanghai 200032

**Abstract:** The energy-transfer process between sodium  $\omega$ -[2-( $\alpha$ -naphthyl)ethoxy]undecanoate (**FP**)<sup>\*</sup> and sodium  $\omega$ -9-anthrylmethyl glutarate (**AFP**) is accelerated by the formation of ESAg when cetyltrimethylammonium chloride (**S16**<sup>+</sup>) has been added to the solvent system of **FP**<sup>\*</sup> and **AFP**. This result is yet another evidence for the formation of ESAg.

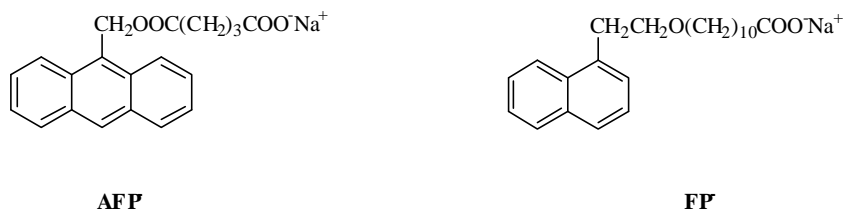
**Keywords:** Energy-transfer process, fluorescence spectra, ESAg.

We have proposed that oppositely-charged long-chain molecules with roughly eight to sixteen carbons might form electrostatically stabilized aggregates (ESAg) by both the hydrophobic-lipophilic interaction (HLI) and the electrostatically attractive force in the concentration range of  $10^{-7}$  mol/L to  $10^{-5}$  mol/L<sup>1,2</sup>. Thus ESAg is yet another structural niche for molecular assemblages in-between the simple aggregate and the micelles. That ESAg species existing at concentrations much lower than the usual CMC (critical micelle concentration) values, *i.e.*, at  $10^{-6}$ - $10^{-4}$  mol/L, was a new concept<sup>1</sup>. There are two lines of evidence for ESAg formation, derived from (1) the coaggregating behavior of cationic or anionic kinetic probes with anionic or cationic surfactants<sup>2</sup> and (2) the coaggregating behavior of the fluorescence probes with oppositely charged surfactants<sup>3</sup>. In experiments of the kinetic probes, the hydrolytic rate constants of the probes were reduced because of ESAg formation. The ESAg concept implies that the ESAg species will naturally grow into the +/- type of mixed micelles made up of comparable amounts of cationic and anionic surfactant molecules. Furthermore, in the experiments of the fluorescence probes, *i.e.*,  $\omega$ -[2-( $\alpha$ -naphthyl)ethoxy] decyltrimethyl- ammonium bromide (**FP**<sup>+</sup>) and sodium  $\omega$ -[2-( $\alpha$ -naphthyl)ethoxy]-undecanoate (**FP**<sup>-</sup>), the formation of intermolecular excimers of the fluorescence probes was observed in the fluorescence spectra because of ESAg formation<sup>3</sup>. In the experiments of a cationic kinetic probe we found that the hydrolytic rate constants did not change when the cationic surfactant was added to the solvent system of the cationic probe because of hydrophilicity of the ionic head group and the electrostatically repelling force. When we extended our research work to two tetrapus molecules, *i.e.*, C [CH<sub>2</sub>O(CH<sub>2</sub>)<sub>3</sub>(CF<sub>2</sub>)<sub>2</sub>O(CF<sub>2</sub>)<sub>2</sub>SO<sub>3</sub><sup>-</sup>Na<sup>+</sup>]<sub>4</sub> and C[CH<sub>2</sub>O(CH<sub>2</sub>)<sub>3</sub>(CF<sub>2</sub>)<sub>4</sub>O(CF<sub>2</sub>)<sub>2</sub>SO<sub>3</sub><sup>-</sup>Na<sup>+</sup>]<sub>4</sub>, which are interesting in host-guest chemistry or supramolecular chemistry, we observed that these two four-armed host molecules with

\* E-mail: jxk@pub.sioc.ac.cn

four anionic end groups could host either cationic or anionic naphthalene fluorescence probes, *i.e.*,  $\text{NpCH}_2\text{CH}_2\text{O}(\text{CH}_2)_{10}\text{N}^+\text{Me}_3\text{Br}^-$  and  $\text{NpCH}_2\text{CH}_2\text{O}(\text{CH}_2)_{10}\text{COO}^-\text{Na}^+$  where Np = naphthyl<sup>4</sup>. However, the inclusion of a cationic probe is much easier than that of an anionic probe. This observation may serve as another demonstration of the importance of electrostatic attraction for ESAg formation in the inclusion process.

Energy transfer is a crucial process in photosynthesis<sup>5</sup>. In the past decades, the mimicry of the energy-transfer process has been attracting the great attention. We now report one new energy-transfer process, which is accelerated by the formation of ESAg. Compounds used in the study are sodium  $\omega$ -[9-anthrylmethyl]glutarate (**AFP**), sodium  $\omega$ -[2-( $\alpha$ -naphthyl)ethoxyl] undecanoate (**FP**<sup>-</sup>) and cetyltrimethylammonium chloride (**S16**<sup>+</sup>).



## Experimental

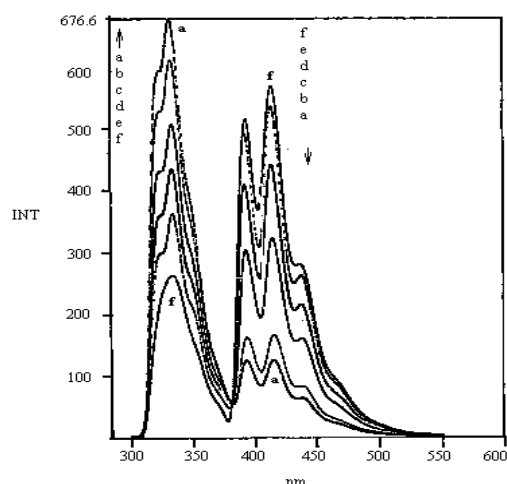
**FP**<sup>-</sup> and **AFP**<sup>-</sup> were synthesized in our laboratory and identified by elemental analysis, <sup>1</sup>H NMR and MS. **S16**<sup>+</sup> was purchased and was purified by recrystallization twice from the mixture solvent, *i.e.*,  $\text{H}_2\text{O}-\text{C}_2\text{H}_5\text{OH}-\text{C}_2\text{H}_5\text{OOCCH}_3$ . Deionized water was used in the experiments. Emission spectra in  $\text{H}_2\text{O}$  at 298 K were recorded by a Perkin-Elmer LS-50 fluorescence spectrometer using the excitation wavelength of 284 nm<sup>3</sup>.

## Results and Discussion

The influence of increasing **S16**<sup>+</sup> concentration on the fluorescence intensities of **FP**<sup>-\*</sup> and **AFP**<sup>-\*</sup> in  $\text{H}_2\text{O}$  at  $\lambda_{\text{ex}} = 284$  nm and  $t = 35^\circ\text{C}$  can be found from **Figure 1**. In **Figure 1** the fluorescence spectra of **FP**<sup>-\*</sup> are shown in the left side at 300 nm to about 380 nm, while the fluorescence spectra of **AFP**<sup>-\*</sup> are shown in the right at about 380 nm to 550 nm. Furthermore, the intensities of **FP**<sup>-\*</sup> were decreased from a to f (left side curves) and the fluorescence intensities of **AFP**<sup>-\*</sup>, which was formed by both the absorption of 284 nm light of **AFP**<sup>-</sup> and the singlet-singlet energy-transfer between **FP**<sup>-\*</sup> and **AFP**<sup>-</sup> in the presence of **S16**<sup>+</sup> (*vide infra*), were increased from a to f (right side curves) when **S16**<sup>+</sup> was added. This result can be attributed to the formation of coaggregates of **FP**<sup>-</sup> and **AFP**<sup>-</sup> with **S16**<sup>+</sup>. In the coaggregates, the energy-transfer between the excited **FP**<sup>-</sup> and **AFP**<sup>-</sup> could occur because the energy of the excited naphthyl is 92 Kcal/mole and the energy of excited anthryl is 76.3 Kcal/mol<sup>6</sup> ( $92 > 76.3$ ). This result is consistent with that of the singlet-singlet energy transfer. In **Figure 1** curve a (right side) indicates the fluorescence of **AFP**<sup>-\*</sup> without **S16**<sup>+</sup>. Tung *et al.* reported that the absorption spectra indicate that for the equimolar mixture of naphthalene labeled molecule and anthracene

labeled molecule more than 95% light at 280 nm is absorbed by the naphthlene labeled molecule<sup>7</sup>.

**Figure 1** Effect of gradually increasing **S16<sup>+</sup>** concentration on the fluorescence intensities of a mixture of **FP<sup>-</sup>** ( $1.0 \times 10^{-5}$  mol/L) and **AFP<sup>-</sup>** ( $1 \times 10^{-5}$  mol/L)



in  $H_2O$  at  $\lambda_{ex} = 284$  nm and  $t = 35^\circ C$ , the concentrations of **S16<sup>+</sup>** ( $\times 10^{-7}$  mol/L) are a) 0.0, b) 1.0, c) 2.0, d) 4.0, e) 6.0, f) 10.0

Thus **AFP<sup>-</sup>** may also absorb a very small amount of 284 nm light and become excited, as shown by curve a (right side) in **Figure 1**. But it is much weaker than that of **FP<sup>-\*</sup>** shown by curve a in the left side. However, it has been demonstrated that **FP<sup>-</sup>** and **AFP<sup>-</sup>** can not form coaggregate at  $10^{-5}$  mol/L because **FP<sup>-</sup>** and **AFP<sup>-</sup>** have the same charge<sup>2</sup>. Therefore, in the absence of added **S16<sup>+</sup>** there is no energy-transfer between **FP<sup>-\*</sup>** and **AFP<sup>-</sup>**. Furthermore, in the aforesaid experiments the range of **S16<sup>+</sup>** concentration is from  $1 \times 10^{-7}$  mol/L to  $1 \times 10^{-6}$  mol/L, which is much smaller than the CMC value of **S16<sup>+</sup>** [ $(2.0 \pm 0.3) \times 10^{-3}$  mol/L] measured in the presence of **FP<sup>-</sup>** ( $1.0 \times 10^{-5}$  mol/L) by the surface tension method. Since the range of **S16<sup>+</sup>** concentration in above-mentioned experiments is much less than its CMC, the formation of **S16<sup>+</sup>** micelle can be excluded.

In conclusion, an energy-transfer process accelerated by the formation of ESAg has been observed. The energy-transfer from **FP<sup>-\*</sup>** to **AFP<sup>-</sup>** occurs only in the presence of **S16<sup>+</sup>**, a result in harmony with the ESAg concept.

## References

1. X. K. Jiang, *Pure and Appl. Chem.*, **1994**, *66*, 1621.
2. a. X. K. Jiang, G.Z. Ji, J. S. Wang, *Chin. Chem. Lett.*, **1991**, *2*, 813.  
b. X. K. Jiang, G. Z. Ji, J. S. Wang, *Chin. Chem. Lett.*, **1992**, *3*, 231.
3. X. K. Jiang, J. S. Wang, *Chin. J. Chem.*, **1993**, *11*, 472.
4. a. J. S. Wang, H. Z. Zhang, W. Y. Huang, X. K. Jiang, *Tetrahedron*, **1994**, *50*, 10459.  
b. X. K. Jiang, J. T. Zhang, *Aggregation and Self-Coiling of Organic Molecules*, Shanghai Science Press, Shanghai, **1996**, pp.136-151.

5. a. K. Sauer, *Ann. Rev. Phys. Chem.*, **1979**, *30*, 155.  
b. G. Peter, C. J. Tredwell, G. F. Searle, W. Barber, *J. Biochem. Biophys. Acta*, **1978**, *501*, 232.
6. G. J. Kavamos, N. J. Turro, *Chem. Rev.*, **1986**, *86*, 401.
7. C. H. Tung, H. F. Ji, *J. Phys. Chem.*, **1995**, *99*, 8311.

Received 14 March, 2001