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Spectral Properties and Solubilization Location of 2'-Ethylhexyl 4-(N,N-Dimethylamino)benzoate in Micelles

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Dual fluorescence and UV absorption of 2'-ethylhexyl 4-(N,N-dimethylamino)benzoate (EHDMA) were investigated in cationic, non-ionic and anionic micelles. When EHDMA was solubilized in different micelles, the UV absorption of EHDMA was enhanced. Twisted intramolecular charge transfer (TICT) emission with longer wavelength was observed in ionic micelles, whereas TICT emission with shorter wavelength was obtained in non-ionic micelles. In particular, dual fluorescence of EHDMA was significantly quenched by the positively charged pyridinium ions arranged in the Stern layer of cationic micelles. UV radiation absorbed mainly decays via TICT emission and radiationless deactivation. The dimethylamino group of EHDMA experiences different polar environments in ionic and non-ionic micelles according to the polarity dependence of TICT emission of EHDMA in organic solvents. In terms of the molecular structures and sizes of EHDMA and surfactants, each individual EHDMA molecule should be buried in micelles with its dimethylamino group toward the polar head groups of different micelles and with its 2'-ethylhexyl chain toward the hydrophobic micellar core. Dynamic fluorescence quenching measurements of EHDMA provide further support for the location of EHDMA in different micelles.

Key words: Dual fluorescence, Twisted intramolecular charge transfer, UV absorption, Surfactant, 2'-Ethylhexyl 4-(N,N-dimethylamino)benzoate, UV absorber, Sunscreen

I. INTRODUCTION

Currently, various ultraviolet (UV) absorbers have been used as sunscreens in sun-care products to avoid UV radiation which can lead to dermatological problems such as sunburn [1], erythema [2], cutaneous photoageing [3] and immunosuppression [4]. In principle, such an excited UV absorber disposes of its excess energy by heat, by luminescence, by interaction with neighboring molecules or by photodegradation [5]. 2'-Ethylhexyl 4-(N,N-dimethylamino)benzoate (EHDMA) is an excellent UV-B absorber (280-320 nm) and frequently used in typical sun-care preparations [6,7]. However EHDMA is an oily liquid and is poorly soluble in water due to its hydrophobic 2'-ethylhexyl chain. The complete solubilization in the finished preparation was needed to improve the efficacy of the sun-care products [7,8]. Moreover, it is also easily oxidated and subject to heat and light [9-11]. As a result, the choice of additives in the formulations should be helpful to improve the solubility and the physicochemical stability of EHDMA in aqueous media.

Surfactants are major components of topical formulations [12-14]. Their micelles are known as microheterogeneous phases in aqueous solution and are capable of incorporating non-polar organic compounds to greatly improve their solubility in aqueous phase [15]. When it is solubilized in micelles, EHDMA will experi-

ence different environments from bulk phase and exhibit dual fluorescence like 4-(N,N-dialkylamino)benzoic acid and its derivatives [16,17]. However EHDMA is a linear molecule with a long flexible and hydrophobic 2'-ethylhexyl chain which may result in different solubilization position and orientation of EHDMA from those of corresponding acid and sodium salt in micelles [18,19]. In this case, micelles may have a special effect on the spectral properties of EHDMA molecules. An approach to the UV absorption of the ground-state EHDMA molecules and the deactivation pathways of the excited EHDMA molecules affords a better understanding of its extensive practical applications. Prior to the present work, the spectral properties of EHDMA in micelles were not described in detail. For this reason, the absorption and dual fluorescence of EHDMA were studied in the presence of typical surfactants in this work. Twisted intramolecular charge transfer (TICT) emission was further used to detect the location of EHDMA in different micelles because it is highly sensitive to the microenvironmental polarity [20-29]. The location of EHDMA in micelles was rationalized in terms of the molecular structures and sizes of EHDMA and surfactants.

II. EXPERIMENTS

EHDMA (>98%) was obtained from Aldrich and used as received. Stock solution of 10.00 mmol/L was prepared by dissolving it in methanol and shielded from light. 0.01 mmol/L EHDMA was used for all measurements. Cyclohexane, *n*-heptane, ethyl

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ether, chloroform, methylene chloride, *iso*-propanol, *n*-propanol, ethanol, acetonitrile, methanol and nitromethane were obtained from Tianjin Reagent Company. Cetyltrimethylammonium bromide (CTMAB) and cetyl pyridinium chloride (CPC) were purchased from Fluka. Polyoxyethylene ($n=10$) lauryl ether (PLE) was obtained from Sigma. Sodium dodecylsulphate (SDS) was supplied by Shanghai Reagent Company and twice recrystallized in ethanol before use. All reagents were of analytical grade. Organic solvents were dried with anhydrous sodium sulfate and redistilled under reduced pressure prior to use. Doubly distilled water was used for all experiments.

Steady state fluorescence was performed on Perkin-Elmer LS-55B luminescence spectrometer with pulse Xenon lamp as excitation light source. Slits for excitation and emission monochromators were 10 nm and 5 nm, respectively. Absorbance was measured with an Agilent 8453 UV-Visible spectrophotometer. Surface tension was determined using a domestic JZ-200 digital tensiometer at 20 ± 0.5 °C. The solubility of EHDMA in pure water was estimated by fluorescence at 20 ± 0.5 °C. Twice distilled water was obtained with a domestic SZ-93 quartz sub-boiled high quality pure water distillatory. Molecular dimensions were estimated by Chem3D software of CambridgeSoft on personal computer.

III. RESULTS AND DISCUSSION

A. Fluorescence of EHDMA in organic solvents

EHDMA is readily soluble in common organic solvents. Figure 1 shows the fluorescence of EHDMA in representative organic solvents. In non-polar cyclohexane, EHDMA only exhibits strong normal fluorescence around 339 nm from its locally excited (LE) state. In the case of methylene chloride, EHDMA shows its typical dual fluorescence. The relatively polar environment results in the bathochromic shift of LE emission with respect to that in cyclohexane [30]. The new anomalous emission around 430 nm, greatly red-shifted with respect to the LE emission around 354 nm, is a clear evidence for TICT process of EHDMA. Furthermore a distinct dual fluorescence appears in acetonitrile. The polar environment results in the larger bathochromic shift of TICT emission. In polar methanol, the dual fluorescence of EHDMA can also be observed but the quantum yield of the LE emission around 354 nm and the TICT emission around 510 nm is lower. Weaker TICT emission with longer wavelength can presumably be ascribed to the stabilization of the highly polar TICT state by the strong dipole-dipole interaction with methanol molecule which results in a rapid non-radiative transition to the ground state [31,32]. Figure 2 illustrates the relationship between Stoke's shift of EHDMA and orientation polarizability of solvents

based upon the Lippert equation [30]. A good linearity directly indicates that TICT emission of EHDMA greatly depends on the environmental polarity.

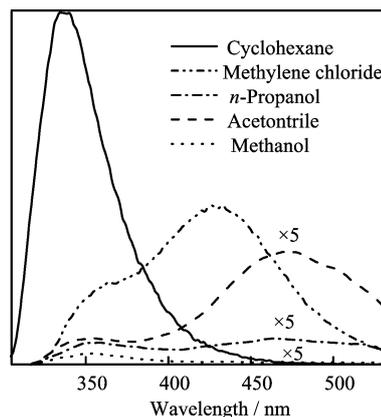


FIG. 1 Fluorescence of EHDMA in organic solvents.

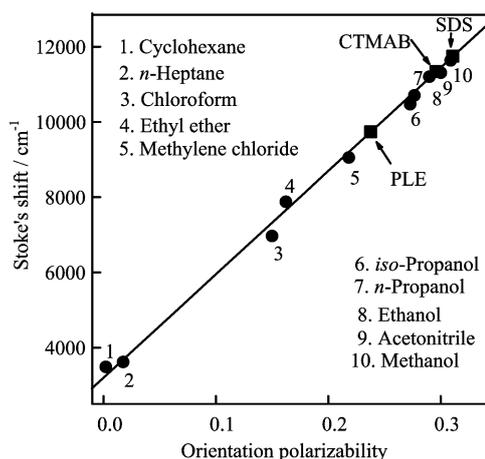


FIG. 2 Dependence of Stoke's shift on orientation polarizability of solvents.

B. Fluorescence of EHDMA in aqueous solution

Fluorescence of EHDMA was further examined in binary mixture of methanol and water in order to study the spectral behavior of poorly soluble EHDMA in aqueous phase. As shown in Fig.3, addition of water to methanol results in a remarkable decrease in dual fluorescence intensity as long as the water content is lower than 50% (V/V) in methanol. In 50% water/methanol mixture, highly polar water results in a greater bathochromic shift of LE and TICT emission than that in methanol. EHDMA exhibits much lower dual fluorescence with its LE emission around 360 nm and with its TICT emission around 520 nm. The weak TICT band can possibly be explained as the stabilization of the highly polar state by strong dipole-dipole in-

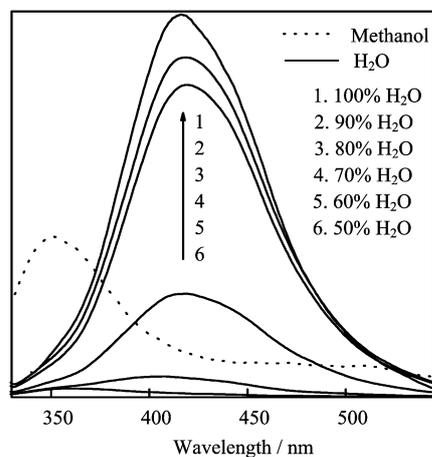


FIG. 3 Fluorescence of EHDMA in binary mixture of methanol and water.

teraction with water molecule and rapid non-radiative transition to the ground or low-lying triplet state [33]. Thereafter further addition of water to methanol can lead to the appearance of a new broad fluorescence at 414 nm with different excitation wavelength from dual fluorescence. This phenomenon suggests that a new ground-state species occurs in aqueous solution. The relative intensity rapidly increases with increasing volume ratio of water to methanol. EHDMA gives rise to the most significant fluorescence at 414 nm in pure water. On the basis of corresponding absorption spectra as shown in Fig.4, the zero baseline is still present in visible region for EHDMA in methanol with 60% and 70% water. These spectral profiles clearly demonstrate that EHDMA is completely soluble. Therefore the broad fluorescence at 414 nm should be assigned to aggregates of EHDMA in view of the molecular structure and the poor solubility (0.21 mg/L) of EHDMA in water. In the case of water content higher than 80% in methanol, the increasing background absorption in visible region directly indicates that EHDMA is not completely dissolved in this case and is dispersed in water/methanol.

C. Absorption of EHDMA in micellar solution

The aggregation of EHDMA in water phase can further be detected by its absorption spectra in micellar solution. Figure 5 exhibits the effect of CTMAB on the absorption of EHDMA in aqueous solution. Two absorption maxima could be observed at 315 nm and 345 nm in pure water. High background absorption appears in UV and visible regions. These results reflect that EHDMA is not completely soluble in water as described above. The absorbance at 315 nm increases and that at 345 nm decreases with increasing concentration of CTMAB. At the critical micellar concentration (CMC) of CTMAB, EHDMA almost shows

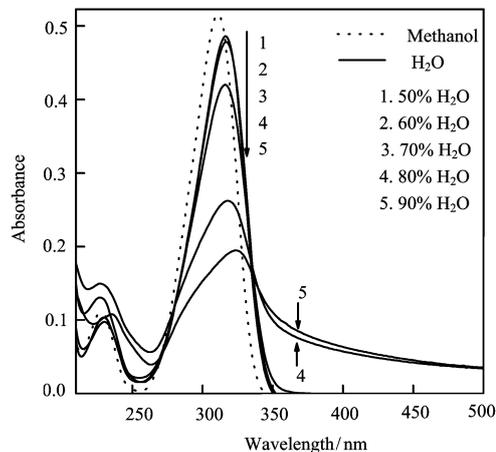


FIG. 4 Absorption of EHDMA in binary mixture of methanol and water.

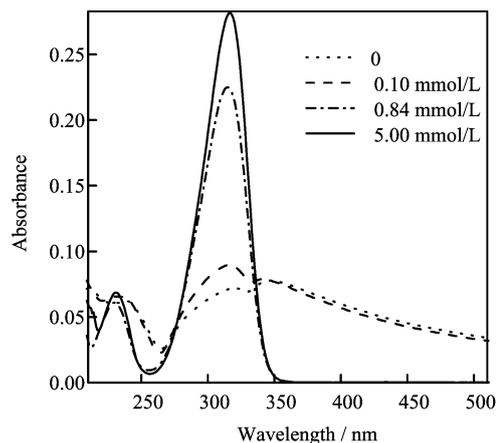


FIG. 5 Effect of CTMAB on absorption of EHDMA in aqueous solution.

negligible absorption at 345 nm. The absorbance at 315 nm greatly increases at the same time. The zero baseline also occurs in the visible region. These phenomena can be attributed to complete solubilization of EHDMA in micellar solution of CTMAB. In this case, EHDMA aggregates dissociate and individual EHDMA molecule is present in CTMAB micelles. As a result, the aggregation of EHDMA should be responsible for the absorption at 345 nm. This result provides additional evidence for the conclusion obtained by the fluorescence and the absorption measurements in binary mixture of water and methanol. Similar spectral behavior was also observed in the presence of CPC, PLE, and SDS.

D. Fluorescence of EHDMA in micellar solution

EHDMA shows very different fluorescence in micellar solution from that in water. Figure 6 shows the effect of CTMAB on the fluorescence of EHDMA in aqueous

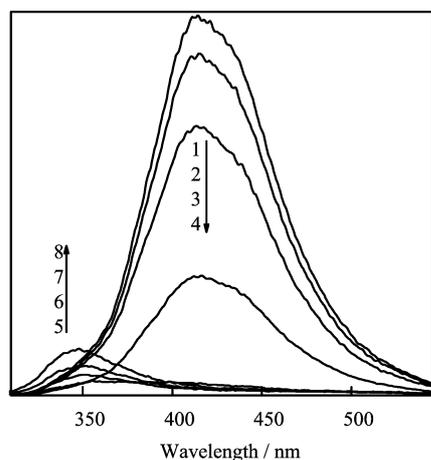


FIG. 6 Effect of CTMAB on fluorescence of EHDMA with different concentration of 0, 0.05, 0.10, 0.20, 0.50, 1.00, 2.00, and 5.00 mmol/L from 1 to 8 as indicated in the figure in aqueous solution.

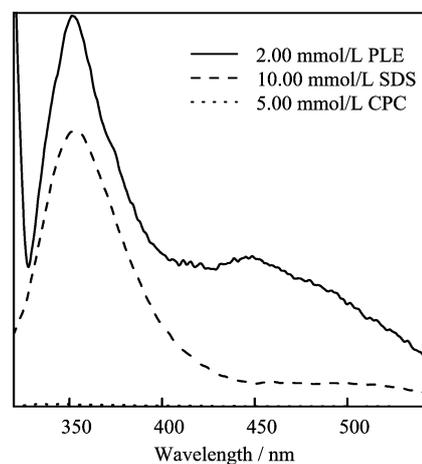


FIG. 7 Effect of CPC, PLE, and SDS on fluorescence of EHDMA in aqueous solution.

solution. The fluorescence intensity at 414 nm rapidly decreases with increasing concentration of CTMAB. When the CTMAB concentration reaches its CMC (0.84 mmol/L), the fluorescence of EHDMA aggregates disappears accompanied by the appearance of LE emission around 350 nm and TICT one around 490 nm. The solubilization of EHDMA in CTMAB micelles should be responsible for this phenomenon, consistent with the result obtained by absorption measurements. The dimethylamino group of EHDMA should be positioned in a polar microenvironment according to the polarity dependence of TICT emission as shown in Fig.2. In CPC micelles, as shown in Fig.7, EHDMA exhibits negligible dual fluorescence although CPC has the same cetyl chain as CTMAB and should have a similar effect on dual fluorescence of EHDMA like CTMAB. This phenomenon suggests that the pyridinium cation of CPC quenches the dual fluorescence of EHDMA. The experimental result provides a direct evidence for the location of the dimethylamino group in the proximity of the pyridinium cation and in a polar microenvironment in CPC micelles. In the case of SDS micelles, the TICT emission appears with longer wavelength (~500 nm) than that in CTMAB micelles, indicating that the dimethylamino group is also located in a polar environment. However, the TICT emission of EHDMA blue-shifts to 446 nm in PLE micelles compared with that in CTMAB and SDS micelles. The spectral change in dual fluorescence clearly indicates that the dimethylamino group was situated in a less polar microenvironment according to the polarity dependence of TICT emission.

E. Fluorescence quenching of EHDMA in micelles

Fluorescence quenching measurements were further studied in order to examine the location of the aromatic moiety of EHDMA in micelles. In homogeneous solution, dynamic fluorescence quenching by a quencher (Q) conforms to the Stern-Volmer equation, $I_0/I=1+K_{SV}[Q]$ (where K_{SV} is the dynamic quenching rate constant, I_0 and I is the fluorescence intensity in the absence and the presence of quencher, respectively). Considering the cationic, non-ionic and anionic surfactants employed in the experimental, the neutral nitromethane molecule was selected as a quencher to avoid electrostatic interaction between the micelle-water interface and a quencher. Figure 8 shows Stern-Volmer plots of I_0/I as a function of $[CH_3NO_2]$ for EHDMA in CTMAB, SDS and PLE micelles. Stern-Volmer constants obtained for EHDMA in different mediums of H₂O/methanol, CTMAB, PLE, and SDS were 38.18 ± 0.53 , 28.99 ± 0.44 , 27.31 ± 0.45 , and 25.74 ± 0.56 L/mol, respectively. EHDMA was shielded from the quencher CH₃NO₂ in different micelles to some extent. More significant fluorescence quenching of EHDMA by CH₃NO₂ molecules was observed in SDS micelles than that in CTMAB micelles, indicating that there is a relatively stronger interaction of the aromatic moiety of EHDMA in SDS micelles with CH₃NO₂ molecules in bulk phase. On the contrary, less fluorescence quenching by CH₃NO₂ molecules was detected in PLE micelles compared to that in CTMAB micelles. Thus the aromatic moiety of EHDMA was shielded from CH₃NO₂ molecules in bulk phase to a greater extent. This result provides an evidence for the deep inclusion of the aromatic moiety of EHDMA in PLE micelles.

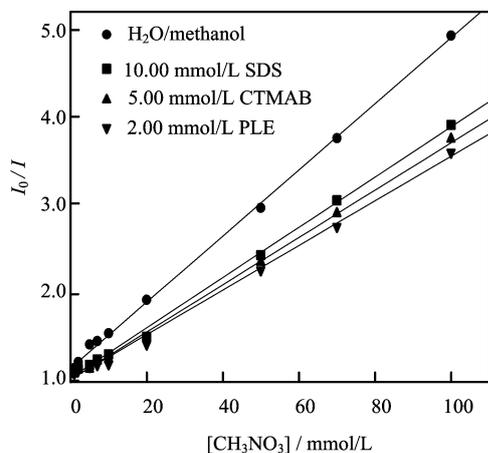


FIG. 8 Stern-Volmer plots of I_0/I vs. $[\text{CH}_3\text{NO}_2]$ for EHDMA in water and micelles.

F. Location and dual fluorescence dependence of EHDMA in micelles

It has been established that the environment in micellar cores is basically similar and the polarity and the diffusion of water molecules gradually decrease from the micelle-water interface to the micellar core [15]. TICT emission can be employed to study the location of EHDMA in different micelles because it is strongly dependent on medium polarity (Fig.2). Like the dissolution of EHDMA in methanol, the solubilization of EHDMA in CTMAB, CPC, PLE, and SDS micelles results in the disappearance of the fluorescence from EHDMA aggregates. In CTMAB and CPC micelles, the linear EHDMA molecule (length $(L)/\sim 16.7 \text{ \AA}$) could be dipped into the micellar core by the hydrophobic interaction because it is shorter than the cetyl chain ($L/\sim 20.2 \text{ \AA}$) of CTMAB and CPC molecules. However the microenvironment surrounding the dimethylamino group of EHDMA is similar to that between ethanol and acetonitrile according to the polarity dependence of TICT emission as shown in Fig.2. The polar environment results in a stabilization of highly polar TICT state and a rapid non-radiative transition [17]. Thus weak TICT emission around 490 nm appears in CTMAB micelles. Furthermore it is energetically favorable for the linear EHDMA molecule to insert in the pallid layer of micelles with its flexible and hydrophobic 2'-ethylhexyl chain towards the micellar core [15]. For these reasons, an individual EHDMA molecule would be located in the micelles with its dimethylamino group toward the micelle-water interface. According to such an arrangement, the positively charged pyridinium ions in the Stern layer of CPC micelles can significantly quench the dual fluorescence of EHDMA because the pyridinium cation is a strong electron-accepting group [34]. This conclusion is in good agreement with the experimental results. Thus, the differences in TICT emission intensity and wavelength provide a way to es-

tablish the location and the orientation of EHDMA in micelles.

In SDS micelles, the EHDMA molecule is slightly longer than the decyl chain ($L/\sim 15.0 \text{ \AA}$) of SDS molecule and the dimethylamino group may be exposed to the polar head groups and experiences more polar environment compared to that in CTMAB micelles. As shown in Fig.2, the microenvironmental polarity around the dimethylamino group is close to that of methanol. Such an arrangement could decrease the energy gap between TICT and ground states, increase the rate of non-radiative processes and thus lead to the attenuated TICT emission with longer wavelength [31,32]. In this case, EHDMA is also easily affected by CH_3NO_2 quencher molecules in bulk phase. In PLE micelles, the dimethylamino group is located in the intermediate microenvironment like that between methylene chloride and *iso*-propanol according to the polarity dependence of TICT emission as shown in Fig.2. The dimethylamino group experiences less polar microenvironment in PLE micelles than that in CTMAB and SDS micelles. In terms of molecular structure and sizes of EHDMA and PLE, the dimethylamino group may be located at the intersection between hydrophilic and hydrophobic moieties of PLE. Such an environment will increase the energy gap between the TICT and the ground states and decrease the rate of non-radiative processes to some extent [31,32]. As a result, the TICT emission should blue-shift and the relative intensity should increase. This is supported by the hypsochromic shift and the enhancement of TICT emission in PLE micelles with respect to that in CTMAB and SDS micelles. Furthermore it is difficult for CH_3NO_2 molecules to penetrate into PLE micelles and to quench the fluorescence of EHDMA because the shell of polyoxyethylene chain is thick in PLE micelles [15]. The structural analyses provide a plausible explanation for the experimental results.

IV. CONCLUSION

The results described here clearly demonstrate that the linear EHDMA molecule was solubilized in CTMAB, CPC, PLE and SDS micelles. UV absorption of EHDMA was enhanced. UV radiation absorbed mainly decays via TICT emission and radiationless deactivation. Therefore the LE emission intensity greatly decreases. In these micelles EHDMA is shielded from external neutral quenchers to some extent. The dimethylamino group experiences different polar environments in ionic and non-ionic micelles. The TICT emission measurements and the structural analyses suggest that the 2'-ethylhexyl chain of EHDMA should be deeply buried in the micellar core and the dimethylamino group exposed to the micelle-water interface. Such an arrangement is different from that of 4-(N,N-dimethylamino)benzoic acid and its sodium salt

in ionic micelles. These conclusions are very significant for a deeper understanding of the UV-absorbing and deactivation processes and the extensive practical applications of EHDMA in sun-care products.

V. ACKNOWLEDGMENT

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- [1] A. Ziegler, A. S. Jonason, D. J. Leffell, J. A. Simon, H. W. Sharma, J. Kimmelman, L. Remington, T. Jacks, and D. E. Brash, *Nature* **372**, 773 (1994).
- [2] N. Kollias, G. N. Stamatias, and J. L. Youn, *Photochem. Photobiol.* **74**, 471 (2001).
- [3] M. Wlaschek, I. Tantcheva-Poor, L. Naderi, W. J. Ma, L. A. Schneider, Z. Razi-Wolf, J. Schuller, and K. Scharffetter-Kochanek, *J. Photochem. Photobiol. B* **63**, 41 (2001).
- [4] M. Ichihashi, M. Ueda, A. Budiyanto, T. Bito, M. Oka, M. Fukunaga, K. Tsuru, and T. Horikawa, *Toxicology* **189**, 21 (2003).
- [5] S. Scalia, A. Casolari, A. Iaconinoto, and S. Simeoni, *J. Pharm. Biomed. Anal.* **30**, 1181 (2002).
- [6] GB7916-87, National standard for the People's Republic of China: Sanitary standard for cosmetics.
- [7] W. Johncock, *Cosmet. Toil.* **114**, 75 (1999).
- [8] S. Scalia, S. Villani, and A. Casolari, *J. Pharm. Pharmacol.* **51**, 1367 (1999).
- [9] M. M. Rieger, *Cosmet. Toil.* **112**, 65 (1997).
- [10] L. R. Gaspar and P. M. B. G. Maia Campos, *Int. J. Pharm.* **307**, 123 (2006).
- [11] N. Serpone, A. Salinaro, A. V. Emeline, S. Horikoshi, H. Hidaka, and J. Zhao, *Photochem. Photobiol. Sci.* **1**, 970 (2002).
- [12] P. Ashton, J. Hadgraft, and K. A. Walters, *Int. J. Pharm.* **87**, 265 (1992).
- [13] M. J. Cappel and J. Kreuter, *Int. J. Pharm.* **69**, 143 (1991).
- [14] R. Alvarez-Roman, G. Barre, R. H. Guy, and H. Fessi, *Euro. J. Pharm. Biopharm.* **52**, 191 (2001).
- [15] G. X. Zhao, *Physical Chemistry of Surfactants*, Beijing: Beijing University Press, 151 (1984).
- [16] Y. B. Jiang, X. J. Wang, M. G. Jin, and L. R. Lin, *J. Photochem. Photobiol. A* **126**, 125 (1999).
- [17] Z. R. Grabowski, K. Rotkiewicz, and W. Rettig, *Chem. Rev.* **103**, 3899 (2003).
- [18] Y. B. Jiang, J. G. Xu, and X. Z. Huang, *Chem. J. Chin. Univ.* **15**, 552 (1994).
- [19] Y. B. Jiang, M. G. Jin, and J. G. Xu, *Spectrosc. Lett.* **29**, 751 (1996).
- [20] S. Kundu, S. Maity, S. C. Bera, and N. Chattopadhyay, *J. Mol. Struct.* **405**, 231 (1997).
- [21] G. Krishnamoorthy and S. K. Dogra, *J. Colloid Interface Sci.* **53**, 213 (1999).
- [22] S. Panja, P. Chowdhury, and S. Chakravorti, *Chem. Phys. Lett.* **368**, 654 (2003).
- [23] P. Hazra and N. Sarkar, *Chem. Phys. Lett.* **342**, 303 (2001).
- [24] S. Panja and S. Chakravorti, *Chem. Phys. Lett.* **367**, 330 (2003).
- [25] Y. B. Jiang, *J. Photochem. Photobiol. A* **88**, 109 (1995).
- [26] H. S. Banu, K. Pitchumani, and C. Srinivasan, *J. Photochem. Photobiol. A* **131**, 101 (2000).
- [27] S. Panja, P. R. Bangal, and S. Chakravorti, *Chem. Phys. Lett.* **329**, 377 (2000).
- [28] Y. Matsushita, T. Suzuki, T. Ichimura, and T. Hikida, *J. Phys. Chem.* **108**, 7490 (2004).
- [29] A. Banerjee, B. Sengupta, S. Chaudhuri, K. Basu, and P. K. Sengupta, *J. Mol. Struct.* **794**, 181 (2006).
- [30] G. Z. Chen, X. Z. Huang, Z. Z. Zheng, J. G. Xu, and Z. B. Wang, *Principles of Fluorescence Spectroscopy, 2nd Edn.*, Beijing: Science Press, 76 and 115 (1990).
- [31] J. M. Hick, M. T. Vandersall, Z. Barbarogic, and K. B. Eisenthal, *Chem. Phys. Lett.* **135**, 413 (1987).
- [32] A. Nag, R. Dutta, N. Chattopadhyay, and K. Bhattacharyya, *Chem. Phys. Lett.* **157**, 83 (1989).
- [33] A. Nag, T. Chakraborty, and K. Bhattacharyya, *J. Phys. Chem.* **94**, 4203 (1990).
- [34] S. Hashimoto and J. K. Thomas, *J. Am. Chem. Soc.* **107**, 4655 (1985).