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Light-responsive multillamellar vesicles in coumaric acid/alkyldimethylamine oxide binary systems: Effects of surfactant and hydrotrope structures

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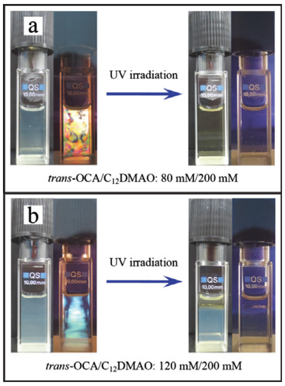
GRAPHICAL ABSTRACT



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ABSTRACT

Herein, we report a series of novel light-responsive multilamellar vesicles based on the surfactant/hydrotrope binary systems. The phase behaviors of alkyldimethylamine oxide (C_mDMAO, $m = 10, 12, 14$) and *trans*-coumaric acid (*trans*-CA) isomerides, including *trans*-ortho-coumaric acid (*trans*-OCA), *trans*-meta-coumaric acid (*trans*-MCA) and *trans*-para-coumaric acid (*trans*-PCA), show that the multilamellar vesicle (MLV) formation region is commonly presented in the *trans*-CA/C_mDMAO systems except *trans*-PCA/C_{12}DMAO. Moreover, the molecular structures of C_mDMAO and *trans*-CA affect the multilamellar vesicle formation region significantly. Generally speaking, the bigger the *m*, the larger the MLV region. Various techniques such as rheology, polarized optical microscopy (POM), ^{1}H NMR, ^{2}H NMR, cryogen transmission electron microscopy (cryo-TEM) and freeze-fracture transmission electron microscopy (FF-TEM) are used to characterize the aggregate structures. The multilamellar vesicles can transform into a homogeneous and transparent micelle phase or a two-phase system in the *trans*-OCA/C_mDMAO binary systems under UV light irradiation, which depends on the chain length of C_mDMAO and the molar ratio of [*trans*-OCA]/[C_mDMAO]. Specifically, the light-stimuli response of multilamellar vesicles in the *trans*-OCA/C_{12}DMAO system is representatively studied in detail. UV–vis spectra and ^{1}H NMR measurements illustrate that the light-induced *trans*-OCA to *cis*-OCA isomerization is essential during the transitions and the light-induced two-phase formation is attributed to the enrichment of surfactants, because the *trans*-*cis* isomerization can not only strengthen the hydrophilicity of *cis*-OCA but also increase the steric

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hindrance between *cis*-OCA and C_{12}DMAO, and thereby altering the morphology of aggregate and the rheological response of bulk phase significantly.

1. Introduction

Generally, the development of stimuli-responsive smart materials is one of the most attractive topics in material science due to their great interests in relating technique fields. These external stimuli could be pH [1–3], CO_2 [4–6], temperature [7,8], light [9–12], redox [13,14], and so on. It is well established that surfactants commonly form aggregates in both polar and apolar solvents, *i.e.* water and alkane, respectively, with different morphologies. Generally speaking, spherical micelles, wormlike micelles and vesicles can be formed in the diluting solution and even liquid-crystalline phases will be formed in the concentrated one [15,16], which relates to the molecular structure of surfactant strongly. As a result, the physicochemical properties of the bulk phase, including viscosity, turbidity and birefringence, will be determined by the micro-structures of aggregates. These self-assembled structures can be responded to various external stimuli through chemically introducing stimuli-responsive moiety in surfactant molecules or adding responsive chemicals to the system directly [17]. Up to now, the aggregate transitions between vesicles and micelles or wormlike micelles and spherical/rodlike micelles have been realized by external stimuli [1–14], which benefits their applications strongly.

Light is one of the most interesting external stimuli because it provides a disturbing way to change physicochemical properties significantly without varying the composition [18–20]. Accordingly, light-responsive moieties and chemicals such as azobenzene, stilbene, naphthopyran, merocyanine, cinnamic acids and its derivatives are widely employed in developing light-responsive systems [18–22]. For example, the cinnamic acid derivative, *trans*-ortho-methoxycinnamic acid (OMCA), was used to develop both light-induced thinning or thickening fluids together with different surfactants such as trimethylammonium bromide (CTAB) [23] and erucyl dimethyl amidopropyl betaine (EDAB) [24], respectively, owing to the *trans-cis* isomerization of OMCA induced transitions between wormlike micelle and rodlike micelle. In the past decades, the dominant works are focused on the diluting solutions and the major transitions are happened among spherical micelles, rodlike/wormlike micelles, and vesicles. Indeed, anisotropic aggregates such as multilamellar vesicles, lamellar and hexagonal phases can also be formed in the concentrated solutions [15,16]. However, the corresponding stimuli-responses are rarely concerned though they strongly benefit to various applications including biological process, mesoporous materials and catalysts fabrication, polymerization, and drug-controlled release [25–27]. In comparison with the stimuli-responsive aggregate transitions in the dilute solutions, the difficulty to study the responsive transitions in the concentrated ones can be appreciated.

Tangso et al. reported the reversible transition between inverse cubic phase and hexagonal phase by employing amphiphilic spiropyran derivatives based on the light-induced isomerization of spiropyran moiety between closed “spiro” form and open “merocyanine” form [28]. Similarly, Peng et al. studied the light-induced reversible transition between hexagonal phase and spherical micelle in the aqueous solution based on the synthesized azobenzene amphiphiles, which provided a new insight into controlling the fluid viscosity [29]. Alternatively, Hao et al. realized the UV light induced multilamellar vesicles to wormlike micelles transition based on the binary mixtures of tetradecyldimethylamine oxide (C_{14}DMAO) and *trans*-para-coumaric acid (*trans*-PCA) [30]. Though the light-response was occurred only in a very narrow concentration region around 60 mM of *trans*-PCA and 150 mM of C_{14}DMAO, however, the work provided an evidential example to develop responsive anisotropic aggregates based on the surfactant/hydrotrope binary mixtures. Accordingly, Yu et al. developed the light-responsive hexagonal phases in the salt-free systems of 1-dodecyl-3-methylimidazolium bromide (C_{12}mimBr)/*trans*-cinnamate (*trans*-CA) and C_{12}mimBr/*trans*-PCA recently [31], whereas the hexagonal phases were remained after UV light irradiation with only slight change in the packing lattice space. Obviously, the route based on the surfactant/hydrotrope binary mixtures in designing responsive anisotropic aggregates is still suffering from some shortcomings especially the sensitivity of the response, *i.e.*, the narrow responsive region [30] and the limited structural changes [31], which is detrimental to their applications. Therefore, developing responsive anisotropic materials with high sensitivity is of particular interest and challenge.

The major motivation of the present work is to develop a new category of light-responsive anisotropic aggregates, multilamellar vesicles, with a widely responsive region based on the surfactant/hydrotrope binary systems, and to establish the structure-property relationships of them. Herein, alkyldimethylamine oxide (C_mDMAO, $m = 10, 12, 14$) and *trans*-coumaric acid (*trans*-CA) isomerides, including *trans*-ortho-coumaric acid (*trans*-OCA), *trans*-meta-coumaric acid (*trans*-MCA) and *trans*-PCA, are employed as surfactants and hydrotropes according to Hao’s work [30], respectively. In this work, the multilamellar vesicle formation regions are well established based on the phase behavior studies, and the structural effects of both surfactants and hydrotropes are considered in detail. Moreover, the light stimuli-responses of multilamellar vesicles as well as the transition mechanisms are studied systematically by various techniques including UV–vis spectra, ^{1}H NMR, ^{2}H NMR, rheology, polarized optical microscopy (POM), cryogen transmission electron microscopy (cryo-TEM) and freeze-fracture transmission electron microscopy (FF-TEM). The present work not only provides new insights into the rheological response of multilamellar vesicles due to the *trans-cis* isomerization of coumaric acid and diversifies the stimuli-responsive fluids, but also provides detailed information about the molecular interactions and structure-property relationships of surfactant/hydrotrope binary systems, which is fundamental importance in designing new responsive surfactant systems and extending their applications in relating fields.

2. Experimental

2.1. Chemicals

Alkyldimethylamine oxide (C_mDMAO, $m = 10, 12, 14$) was synthesized according to Scheme S1 (supporting Information). Decyldimethylamine (98%), dodecyldimethylamine (97%), tetradecyldimethylamine (90%), *trans*-ortho-coumaric acid (*trans*-OCA) (98%), *trans*-meta-coumaric acid (*trans*-MCA) (99%) and *trans*-para-coumaric acid (*trans*-PCA) (98%) were purchased from J&K CHEMICA Company (China). H_2O_2 (30%) was obtained from Shanghai Chemical Co. Ltd., China. The ultrapure water (Millipore) was used.