

Photoelectrochemical Control of Solution Viscosities Using Switchable Amphiphiles

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Amphiphilic molecules form various kinds of molecular assemblies such as micelles, worm-like micelles, and vesicles in aqueous solutions, depending on the geometrical structure and hydrophilic – hydrophobic balance of the molecules. These molecular assemblies have many interesting functions. For example, these assemblies can encapsulate water-insoluble substances in their hydrophobic interior (*solubilization*). In addition, formation of worm-like micelles drastically increases solution viscosity due to entanglement of the assemblies. If the formation and disruption of these molecular assemblies can be controlled by external stimulation, e.g., light irradiation or redox reactions, it can be applied for drug delivery system (DDS) and control of perfume volatilization. In this study, we report reversible control of solution viscosity using a “photoelectrochemically switchable” cationic amphiphile.

i) Photochemical control of viscosity

We used a cationic amphiphile modified with azobenzene moiety, 4-butylazobenzene-4'-(oxyethyl)trimethylammonium bromide (AZTMA)¹⁾, as a photoswitchable amphiphile. AZTMA undergoes reversible *trans* / *cis* photoisomerization upon irradiation of UV and visible light. Critical micelle concentrations (cmc) of *trans* and *cis* AZTMA determined by the specific conductivity measurement were 2.7 mM and 8.2 mM, respectively.

Cetyltrimethylammonium bromide (CTAB), one of the typical cationic amphiphile, form worm-like micelles in the presence of organic counter ions such as sodium salicylate (NaSal) and solution viscosity drastically increases. In this study, photo-responsive AZTMA was incorporated in this worm-like network of CTAB and the effect of photo irradiation on viscosity was studied. Viscosity of CTAB/NaSal solutions increased by the addition of *trans* AZTMA. However, after UV light irradiation to these solutions (formation of *cis* AZTMA), the viscosity decreased with an increase in AZTMA concentration (Figure). Photochemical control of viscosity was thus made possible and the degree of viscosity change was more than thousand times in the optimum condition.

ii) Electrochemical control of viscosity

We report a novel system that enables us to dynamically control the viscoelasticity of fluids by applied electric potential. The system used is a promising candidate for new electro rheological (ER) fluid which will widely be applied to the active controlled release of substances such as dyes and

perfumes, ink for inkjet printers, clutch for transmission. Our system is based on a redox-switchable ferrocenyl surfactant [(11-ferrocenylundecyl)trimethylammonium bromide, FTMA^{2,3)}] that self-assembles into worm-like micelles in the presence of sodium salicylate (NaSal). An aqueous solution of mixed FTMA (reduced form) and NaSal exhibits a remarkable viscoelasticity due to the three-dimensional network consisting of worm-like micelles. After the oxidation of FTMA, the viscosity of the system dramatically decreases and the elasticity disappears. This remarkable viscoelasticity decrease is caused by a significant change in the aggregation state from worm-like micelles to monomers and/or other smaller aggregates due to the enhanced hydrophilicity of FTMA.

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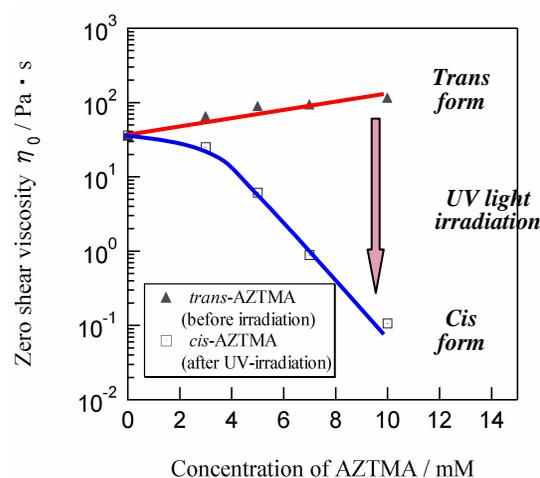


Figure 1 Effect of light irradiation on viscosity of CTAB/NaSal/AZTMA solutions

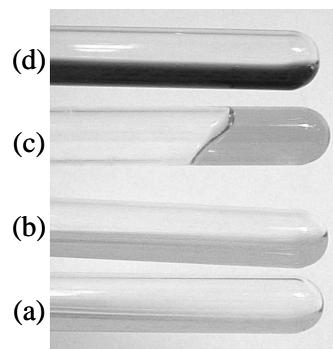


Figure 2 Photograph showing the appearance of aqueous FTMA/NaSal mixture tilted by 90° at a fixed FTMA concentration of 50mM. Samples (a), (b), and (c) are aqueous FTMA(reduced form)/NaSal mixtures at molar ratios of [NaSal]/[FTMA]=0, 0.2, and 0.4, respectively. Sample (d) is aqueous FTMA/NaSal mixture at molar ratio of [NaSal]/[FTMA]=0.4 after potentiostatic electrolytic oxidation.

