Giant vesicles (GV) in colloidal system under the optical polarization microscope (OPM)

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ABSTRACT

This paper discusses the unprecedented microscopic findings of micellar growth in colloidal system (CS) of catalyzed piperidinolysis of ionized phenyl salicylate (PS−). The giant vesicles (GV) was observed under the optical polarization microscope (OPM) at [NaX] = 0.1 M where X = 3-isopropC6H4O−. The conditions were rationalized from pseudo-first-order rate constant, kobs of PS− of micellar phase at 31.1 × 10−3 s−1 reported in previous publication. The overall diameter of GV (57.6 μm) in CS (CTABr/NaX/H2O)-catalyzed piperidinolysis (where X = 3-isopropC6H4O) of ionized phenyl salicylate were found as giant unilamellar vesicles (GUV) and giant multilamellar vesicles (GMV). The findings were also validated by means of rheological analysis.

1. Introduction

Vesicles are double-layered structures, which usually self-assemble and form an artificial liposome-like architecture (Andreozzi et al., 2010; Chen et al., 2004; Feitosa et al., 2006). The aggregate is due to the self-assembly of surfactant molecules in aqueous solutions (Kaler et al., 1989; Kondo et al., 1995). In the general context of complex fluids, vesicle micelles have received considerable attention from theoreticians and experimentalists for the past decade (Marques et al., 1998; Marques et al., 2003; Tondre and Caillet, 2001). When micelles grow, and become vesicle, the aggregates are much like liposomes which form a lipid bilayer. A lipid bilayer, comprises of two layers of phospholipids; arranged end to end with the hydrophobic layer buried between two layers; as a spherical vesicle, it contains aqueous solution inside the chamber (Velázquez et al., 2007; Defeng et al., 2010; Tanner et al., 2006).

Colloidal system, CS containing CTABr/NaX/H2O-catalyzed piperidinolysis where (X = 3-isopropC6H4O) of ionized phenyl salicylate yield a high growth of micellar self-assembly structure. Taking these facts into consideration, we noted an interesting finding of micellar self-assembly of CS (CTABr/NaX/H2O)-catalyzed piperidinolysis of PS− at NaX = 0.1 M where X = 3-isopropC6H4O−.

2. Materials and methods

2.1. Chemicals

Commercial products of the highest available purity, such as cetlytrimethylammonium bromide, C16H33NMe3Br, phenyl salicylate acid (PSaH), 3-isopropC6H4OH, piperidine (Pip) and all other common chemicals used were of reagent grade. The stock solutions of PSaH = 0.01 M were prepared in acetonitrile to form 0.2 mM phenyl salicylate ions (PS−). The stock solutions (w M) of non-ionic substituted phenols were prepared by adding (w + 0.05 M) sodium hydroxide, NaOH.

2.2. Particle size

Particle size of the micelles were measured using Zetasizer Nano ZS (Malvern Instruments Ltd., United Kingdom) equipped with a 4 mW He-

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Ne laser at 633 nm by employing a dynamic light scattering (DLS) method at a scattering angle of 90°. The four-sided clear fluorescent quartz cuvette of 1 cm path length was used for the particle size analysis. The freshly prepared samples were injected into a 7 mL glass bottle through a 0.45 μm filter prior to measurement. All measurements were scanned for 3 times at 35 ± 1 °C.

2.3. Optical polarising microscope (OPM)

The morphology of the prepared micelles was evaluated by employing Leica optical polarising microscope equipped with image analysis software Leica QWin (Germany). A sample was carefully dropped onto the glass slide and covered with a cover slip. A drop of immersion oil was dropped onto the cover slip and a micrograph was observed under 100 μm conditions.

2.4. Rheological measurement

10 mL samples were prepared by mixing a constant concentration of NaOH = 30 mM, Piperidine = 100 mM, CTABr = 15 mM, PS⁻ = 0.2 mM, 3-EtC₆H₄ONa = 0.10 M at 35 °C for steady-shear rheological measurements. The freshly prepared samples were injected into a 7 mL glass bottle through a 0.45 μm filter prior to measurement. All measurements were scanned for 3 times at 35 ± 1 °C.

3. Results and discussion

3.1. Micellar self-assembly solution in CS where X = 3-isopropC₆H₄O⁻

The determination of micellar structure was analysed for CS (CTABr/NaX/H₂O) of ionized phenyl salicylate (PS⁻) catalyzed piperidinolysis, where X = 3-isopropC₆H₄O⁻. 5 mL of aliquots were freshly prepared to prevent the effects of time on micellar growth. The size of these CS micelles was determined at a temperature of 35 ± 1 °C using particle size analysis. The Optical Polarisation Microscope (OPM) was used to discover the micellar structure of the self-assembly aggregates. The concentration of the CS, CTABr = 15 mM, PS⁻ = 0.2 mM, Piperidine = 100 mM, NaOH = 30 mM were kept at a constant for the entire experimental conditions. A set of concentration was analysed for [3-isopropC₆H₄ONa] = 0–0.18 M to ensure reliable analysis without any fluctuation of results.

Fig. 1 shows the graphical illustration for the unprecedented findings of micellar particle size in diameter (nm) versus [NaX]/M where X = 3-isopropC₆H₄O⁻. The total time taken from sample preparation to the completion of measurement was 5 min. From the observation, the particle sizes of micelles exponentially increased at 0.07 M up to 0.10 M with an apparent decrease at 0.13 M. Within the range of [NaX] = 0.00–0.20 M, the micellar self-assembly sizes were below 1 μm with the exception of [NaX] = 0.10 M. The particle size at [3-isopropC₆H₄ONa] = 0.10 M was 57.6 ± 1.2 μm. The addition of [NaX] promoted the micellar growth up to 0.10 M. However, the size reduction of vesicles after 0.10 M is attributed to vesicle disruption of salts concentration through compressing the double layer of vesicles (Defeng et al., 2010; Tanner et al., 2006).

3.2. Micellar self-assembly structure in CS where X = 3-IsopropylC₆H₅O⁻

Micellar self-assembly structures for X = 3-IsopropylC₆H₅O⁻ at 0.10 M are shown in Fig. 2(a)–(d). The giant vesicle (GV) was observed, at various locations, on the glass slide under the OPM. The microstructural findings coincide with the previous article published elsewhere (Alexander et al., 1996).

Fig. 2(a) and (b) depict a giant multilamellar vesicles (GMV), whereas Fig. 2(c) and (d) show a giant unilamellar vesicles (GUV) in the CS at [PS⁻] = 0.2 mM, [NaOH] = 0.03 M, [Pip] = 0.1 M, [CTABr] = 15 mM and [NaX] = 0.10 M where X = 3-IsopropylC₆H₅O⁻.

Presumably, the increases of the micellar size at [NaX] = 0.10 M, where the particle diameter = 57.6 μm were due to the development of giant vesicles (GV) micelles, also known as swelling phenomena. 3-isopropC₆H₅O⁻ is known for its high hydrophobicity, which is prone to penetrate into the micellar system where 3-isopropC₆H₅O⁻ expels the less hydrophobic counterions, i.e PS⁻, Br⁻ at the head group and caused the swollen micelles to grow (Marques et al., 2003). These conditions lead to the development of GV lipid layer.

Such findings also dictated two types of micellar self-assembly GV structures at [NaX] = 0.10 M; a) giant multilamellar vesicles (GMV) and b) giant unilamellar vesicles (GUV). Figure (a), (b), (c) and (d) were captured at different points on the OPM slides containing [NaX] = 0.10 M. Fig. 2(a) and (b) show giant multilamellar vesicles (GMV). GMV consisted of small vesicle(s) contained within a larger vesicle. Perhaps, GMV was formed from vesicles which trapped inside the GUV structure due to excessive additions of [NaX].

Fig. 1. The graph shows the diameter of micellar self-assembly structure of CS where [CTAB] = 15 mM, [PS⁻] = 0.2 mM, [Pip] = 100 mM, [NaOH] = 30 mM and [NaX] (X = 3-isopropC₆H₄O⁻) within [NaX] range = 0.00–0.18 M.
Fig. 3 In general, shear viscosity ($\eta$) versus shear rate ($\gamma$) plot of viscoelastic micellar system reveals the regions of Newtonian, shear thickening ($\eta$ increases) and shear thinning ($\eta$ decreases) (Qi and Zakin, 2002). Flow curves showing only the Newtonian fluid behavior at $\gamma < 10^3$ s$^{-1}$ with $\eta$ values similar to pure water (1.00 m Pa.s) indicates the presence of spherical micelles (SM) or unilamellar/multilamellar vesicles (Davies et al., 2006). On the other hand, if the flow curves show Newtonian fluid behavior in the initial lower values of $\gamma$ followed by shear thickening ($\eta$ increases) at the higher values of $\gamma$ reveal the presence of rodlike (RM)/wormlike micelles (WM) (Davies et al., 2006). Shear thickening ($\eta$ increases) is expected to be due to the further entanglement of the micelles as more disruption occurs by the rotational rheometer (Magid, 1998; Rao et al., 1987). Fig. 3 shows an absence of shear thinning for the entire rheological analysis of 3-IsopropylC$_6$H$_4$ONa = 0.1 M. The GV showed $\eta_0 = 1.4$ m Pa.s was similar to pure water ($\cong 1.00$ m Pa.s) for GV = 57.6 $\mu$m. The results correspond with the above-mentioned general assumptions that the flow curves showing only the Newtonian fluid behavior at $\gamma < 10^3$ s$^{-1}$ with $\eta$ values are similar to pure water (1.00 m Pa.s) indicating the presence of anisotropic GV in the CS (Fig. 2(a)–(d)). In effect, the rheological analysis has validated the findings of the microscopic evidence of these studies (Qi and Zakin, 2002).

Although the study of micellar growth and evolution has extended to the most profound phase (Giorgio et al., 2016; Can et al., 2016; Tian et al., 2016; Misbah et al., 2015; Sharma et al., 2015), this paper is concerned with the micellar growth when maximum amounts of PS$^-$ were expelled from the micellar hydrophilic regions (headgroups). The selection of the interest concentration for the present experiment was based on the kinetic data of earlier studies (Yusof and Khan, 2011; Khalisanni et al., 2016b) where the nonlinear plots of $k_{obs}$ versus [NaX] reached the maximum level, at which the platonic region was observed and the interest concentration (0.10 M) fell within the range of the maxima nonlinear plot (Yusof and Khan, 2011; Khan et al., 2016; Khan and Ismail, 2010; Khan et al., 2000; Khan et al., 1997; Khalisanni et al., 2016a; Khalisanni et al., 2016b). The platonic region rationalized the value of $k_{obs}$ in water ($k_W$) which is almost equal to the value of $k_{obs}$ of micelles, $k_{id}$ ($k_W = k_{id}$) where the identical symbols and calculations are...
cited therein (Yusof and Khan, 2011; Khan et al., 2010; Khan and Ismail, 2010; Khan et al., 2000; Khan et al., 1997; Khalisanni et al., 2016a; Khalisanni et al., 2016b). The value of $k_{obs}$ for water containing [Pip] = 0.10 M, [NaOH] = 0.03 M in the absence of [CTABr] = 15 mM and [3-isopropC6H4ONa] was found to be $k_0 = 31.1 \times 10^{-3}$ s$^{-1}$ for the presence of PS$^-$ = 0.2 mM in aqueous system (Khalisanni et al., 2016a; Khalisanni et al., 2016b). On the other hand, the value of $k_{obs}$ for micelles ($k_{m}$) for aqueous systems containing [Pip] = 0.10 M, [NaOH] = 0.03 M, [PS$^-$] = 0.2 mM in the presence of [CTABr] = 15 mM and [3-isopropC6H4ONa] = 10 M were found to reach maximum level (plato region) where $k_{m,obs} = 31.1 \times 10^{-3}$ s$^{-1}$. At this level, PS$^-$ were mostly expelled from the micellar region due to the countercation effect of salts (Khalisanni et al., 2016a; Khalisanni et al., 2016b). The platiconic region also indicated the amounts of countermolecules were almost saturated in micellar phase due to its hydrophobicity and solubility in CTABr (Vivek et al., 2006). The effect of hydroxide ions was negligible throughout the entire study since pseudo-first-order rate constants ($k_{obs}$) were not sensitive to OH$^-$ ion catalysis (Khan, 2010).

4. Conclusions

In summary, the unprecedented findings of giant vesicles (GV) under the optical polarization microscopy (OPM), at which GV were found in the formed of giant multimamellar vesicles (GMV) and giant unilamellar vesicles (GUV) in colloidal system (at [PSH] = 0.2 mM, [NaOH] = 0.03 M, [Pip] = 0.1 M, [CTABr] = 0.015 M and [NaX] = 0.10 (where X = 3-isopropylC6H4O$^-$)) has proven that the technique involved is considered to be a rapid method. It has been proven by the total time needed from sample preparation to the completion of measurement; which was only 5 min. The findings of the microscopic analysis and particle size analysis for these studies were also validated by the rheological investigations. The results of these studies are also coherence with the kinetic evidence published elsewhere (Khalisanni et al., 2016b). The recent study might contribute to the investigation of polymer research, micellar-enhanced ultrafiltration system (MEUF) and lipid-protein interactions.

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References


