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Effect of glycolipids on the stability and electrophoretic mobility of decanoic acid vesicles

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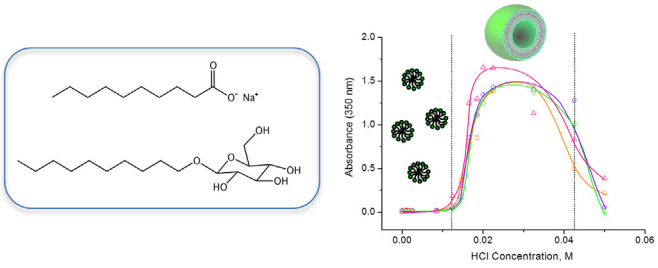
HIGHLIGHTS

- The physico-chemical properties of mixed fatty acid-glycolipids systems have been investigated.
- The stability of fatty acid vesicles is enhanced and improved in the presence of glycolipids.
- Glycolipids have influenced the electrophoretic mobility of fatty acid vesicles.
- Mixed fatty acid-glycolipids vesicles could be used as a new drug carrier system in the future.

GRAPHICAL ABSTRACT



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ABSTRACT

Glycolipids, namely heptyl-β-D-glucopyranoside (HG), octyl-β-D-glucopyranoside (OG) and dodecyl-β-D-glucopyranoside (DG), incorporated in sodium decanoate–decanoic acid (SD–DA) aggregates have been found to affect the critical vesicular concentration (CVC) values and electrophoretic mobility behaviour of their vesicles. Titration of the solutions has shown that the buffering capacity from COO^-...COOH interaction and multilamellar vesicles was predominantly observed under polarized light microscope for the solutions that have been brought down to neutral pH. CVC of the decanoic acid was reduced to half the initial value (0.02 M) when 4% DG was introduced into the solution, while only a slight change was observed when shorter glycolipids were mixed with the decanoic acid. The glycolipids reduced the electrophoretic mobility of the vesicles possessing a strong interaction between the head groups, which belong to the carboxylate of the fatty acid and hydroxyl of the glycolipids, probably suggesting partial neutralization. Thus, the presence of glycolipids in small amounts promotes the formation of decanoic acid vesicles by enhancing the bilayer curvature through hydrogen bonding within the polar region.

1. Introduction

Bilayers formed from mixed amphiphilic molecules have been a pertinent subject for understanding how natural bilayers work, providing barriers and supporting many biochemical activities. Applications of bilayer structures for enzyme entrapment [1] and as vesicles as drugs carriers [2] have been reviewed. Among those reviewed, fatty acid would be a good example of anionic surfactants that can form vesicles.

Titration of fatty acid solutions to form lamellar structure is one of numerous attempts at mimicking the natural. It has been reported that gradients of micellar–vesicles phase transition of decanoic acid have been studied for the kinetic and thermodynamic effects of their vesicles, using dialysis method [3] and encapsulation of salmon testis DNA and catalase [4]. The vesicle stabilization was repeatedly denoted by partial ionization of carboxylic acid groups. The total concentration of the fatty acid may be an indicator of the presence of lamellar, but the ratio of ionization of fatty acid-soaps would describe the variation of self-aggregation structures

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present in different pHs. The "buffering capacity" due to ionization of carboxylic acid groups explains the observed plateaus from the titration profiles. The hydrogen bonding network between ionized fatty acids and respected protonated fatty acid support the formation of the stable vesicles [4]. An earlier report has suggested that a lamellar phase of potassium decanoate has been observed at pH around 7 and at temperatures implied from phase transition profiles [5].

The formation of vesicles or their co-existence from a mix of surfactants also has been investigated, including mixtures of cationic/anionic surfactants [6,7], phospholipid/triacylglycerol/nonionic surfactants [8], and DPPC/octyl glycoside [9]. It has been reported that additional fatty acids in phospholipid vesicles would undergo rapid change and produce larger size of vesicles [10]. Some examples of fatty acids in the presence of lipids have shown aggregation transitions including into lamellar phase, being strongly dependent on temperature and chain length [11]. Inverted hexagonal and non-lamellar phases have been extensively reviewed. Meanwhile, the principle of bilayer formation with lateral force imbalance experienced in a bilayer from the polar head groups, polar head group/hydrophobic interfaces, and the hydrophobic regions have also been discussed [12]. In yet a different report, the addition of co-surfactants has been reported to induce vesicle breakdown [13].

A calculation of spontaneous curvature has suggested that bending rigidity of mixed surfactants has a linear relation with alkyl chain lengths [14]. The classical idea of spontaneous vesicle formation due to external force is similarly important with the spontaneous curvature of bilayers to form different types of vesicles [15]. In the same review, the energetic stabilization of mixed monolayers is closely related to the asymmetric composition of inner and outer layers based on molecular structure, head group charges and length of hydrophobic tail. There is agreement that there is a spontaneous vanishing curvature from flat bilayers into vesicles for mixed monolayers [16]. Bending energy and entropy calculations were used to predict possible phase diagrams.

Furthermore, the addition of co-surfactants certainly alters the aggregation curvature. The self-aggregation of glycolipids and their mixture with various amphiphiles have been discussed based on the interactions and organization within the hydrophilic region of the aggregates [17]. In a recent study, the aggregation of branched-chain glycolipids with different hydrophilic strengths into vesicles has been reported [18]. However, to our knowledge, the participation of glycolipids in fatty acid vesicles is still not yet well documented. In this report, the incorporation of glycolipids within bilayers of decanoic acid (DA) will be presented in the correlation of hydrated phase transition with different pHs and fatty acid concentrations. The electrophoretic mobility would indirectly support the interactions occurring within the head groups of the surfactants.

2. Materials and methods

2.1. Materials

Dodecyl-β-D-glucopyranoside (99%), octyl-β-D-glucopyranoside (99%), heptyl-β-D-glucopyranoside (99%), decanoic acid (99%), sodium hydroxide (98%), disodium hydrogen phosphate dehydrate (≥99%), and hydrochloric acid (with fuming ~36%) were purchased from Fluka. Monosodium dihydrogen phosphate (99%) was purchased from M&B Pronalys* Ar. All chemicals were used as received. All glycolipids and decanoic acid were dried over phosphorus pentoxide in vacuum condition for at least 24 h. Distilled-deionized water with the ionic conductivity of 18.2 μS/cm was used for all sample preparations.

2.2. Sample preparation for phase transitions

A solution of sodium decanoate–decanoic acid (SD–DA) was initially prepared at 0.2 M in 0.25 M NaOH. The solution was divided and diluted into stock solutions that consisted of 0.1 M of SD–DA in 0.125 M NaOH. Appropriate amounts of dodecyl-β-D-glucopyranoside (DG), octyl-β-D-glucopyranoside (OG) and heptyl-β-D-glucopyranoside (HG) were dissolved separately to produce 0.004 M of glycolipids in SD–DA solutions. All four series of samples were then diluted to 0.05 M SD–DA with the addition of different amounts of HCl solution, thus changing the pH of the sample solutions. The concentration of the glycolipids would be 0.002 M to give 25:1 mol ratio of decanoic acid/glycolipid.

2.3. Sample preparation for vesicle formation

All vesicle solutions were prepared in 0.05 M phosphate buffer solutions prepared from 3:2 mol ratio of disodium hydrogen phosphate and monosodium dihydrogen phosphate to maintain the solutions at pH ~ 7. A solution of decanoic acid and NaOH with equal concentrations in 0.05 M phosphate buffer was divided and diluted into stock solutions that consisted of 0.04 M SD–DA. Appropriate amounts of dodecyl-β-D-glucopyranoside (DG), octyl-β-D-glucopyranoside (OG) and heptyl-β-D-glucopyranoside (HG) were then dissolved separately to produce 0.0016 M of glycolipids in SD–DA solutions. A series of samples were then diluted in the range of 0.005 to 0.030 M.

2.4. Determination of phase transitions and vesicle formation

The pH and ionic conductivity of the solutions were measured from a calibrated Cyber Scan PC 510 pH/Conductivity meter. The absorbance of the samples was scanned with a Varian Cary 50 UV-visible spectrophotometer at 350 nm to determine the turbidity and critical vesicular concentration (CVC). The samples were thermostated at 25.0 °C with a Peltier water circulator.

The presence of vesicles in the solutions was observed under optical microscopic images. The images were captured from a Leica DMRXP polarizing light microscope with a magnification of 50x and analyzed with Leica QWin software.

2.5. Determination of electrophoretic mobility

A Rank Brothers Ltd. capillary electrophoresis equipped with a 3 mW helium–neon laser was employed for electrophoretic mobility measurement. The particle movement was directly captured with a Philips CCD video camera connected to a JVC colour monitor. The charge particles in an electrolyte solution moved towards the opposite charge electrode. The migration velocity of the particle was directly proportionate to the applied electrical field. The displacement of the particles was monitored and recorded provided that their size fell within the magnification power of the lens used in the video camera. The migration velocity (ν, m s^{-1}) of a charged particle was given as,

$$\nu = \mu_e E \quad (1)$$

where, μ_e was the electrophoretic mobility (m^2 s^{-1} V^{-1}) and E the applied electrical field (V m^{-1}). Note that μ_e of a charged particle remained constant during the experiment because both the electrical and the frictional forces acting in an electrophoretic set were assumed balanced. The μ_e under these balanced conditions was given as,

$$\mu_e = \frac{q}{6\pi\eta r} \quad (2)$$