Application of cross-linked stearic acid nanoparticles with dialysis membranes for methylene blue recovery

Ming Chen[a], Chad T. Jafvert[a,b,*]

[a] Lyles School of Civil Engineering, Purdue University, West Lafayette, IN 47907, USA
[b] Division of Environmental & Ecological Engineering, Purdue University, West Lafayette, IN 47907, USA

ABSTRACT

The interfacial properties of conjugated linoleic acid (CLA), and the ability to polymerize it, make it a potential precursor to nano-scale materials for water and wastewater treatment. Hence, the properties of CLA and of cross-linked linoleic acid micelles, which are basically stearic acid (SA) nanoparticles, were investigated in this study. The acid dissociation constant (pK_a) of CLA was measured to be 4.93. The surface tension (γ) and the critical micelle concentration (CMC) of CLA (potassium salt) at different temperatures and ionic strengths were measured. Higher temperatures and ionic strengths both led to lower CMC and surface tension values. The average diameter and aggregation number of 4 mM thermally cross-linked micelles (4.55 nm and 135, respectively) were both larger than that of self-assembled 4 mM CLA micelles at 25 °C (2.83 nm and 44, respectively) in 0.1 M KOH. The pure cross-linked SA nanoparticles were obtained by repeated dialysis, and the stability of the cross-linked nanoparticles was confirmed by further dialysis and from equilibration studies in different solvents. The potential application of SA nanoparticles with dialysis membranes was tested by removing a cationic organic material, methylene blue, from water.

1. Introduction

Commercially available conjugated linoleic acid (CLA) is a group of positional and geometric conjugated dienoic isomers of linoleic acid (LA), which also are found in the fat of beef and other ruminants, as well as dairy products [1–3]. The structures of the two major molecules within the CLA mixture which occurs naturally are the cis-9, trans-11, and trans-10, cis-12 structural isomers, shown in Fig. 1. In the past, most research concerning CLA has focused on possible positive effects of CLA to human health, including: anti-carcinogenesis effects, anti-atherosclerosis effects, reduction in the onset of diabetes, improvements in bone health, and reduction in adipose tissue [4–8]. Thus, uses of CLA have been mostly as a food additive or health product ingredient. In general, the interfacial properties of CLA and properties of CLA micelles have been ignored. Previous studies on the morphologies of many fatty acids and their salts under different conditions have been conducted [9–12], with these studies mostly focusing on vesicle formation as a function of pH. Recently, reactivity of the conjugated double bonds and the amphiphilic properties of CLA have attracted the attention of some researchers [13–15]. For example, compared with oleic acid, which contains a single double bond, and linoleic acid, which contains two non-conjugated double bonds, the conjugated double bonds of CLA make polymerization possible. Additionally, by changing the solution properties, nanoparticles of different shapes can be formed which may find potential uses in different fields, including as stable vesicles (i.e., ufasomes) for drug delivery in the pharmaceutical industry [12,13]. In addition, the carboxylic acid functional group of CLA makes it a potential precursor material to synthesize other surfactants that can be polymerized [15]. Further, low-cost, high product yield synthesis strategies for CLA have been developed that make its use cost effective in many fields [14,16].

Depending on the pH, CLA may precipitate at high concentrations rather than form micelles in solution. However, if the pH is adjusted to a high value with a monovalent base (e.g., KOH), essentially all CLA will exist in anionic form, and at concentrations above its CMC value, micelles form preventing precipitation (i.e., due to the solubility product with K^+). The application of surfactant micelles for water treatment has been researched widely. Surfactant micelles, combined with ultrafiltration (UF), have been considered a promising separation technology [17–23]. The rejection of the nano-scale micelles by UF membranes leads to the removal of ionic contaminants associated with the charged surface of the micelles, and removal of neutral organic molecules that may solubilize within the organic core of the micelles [18]. An obvious shortcoming of this technology is the passing of
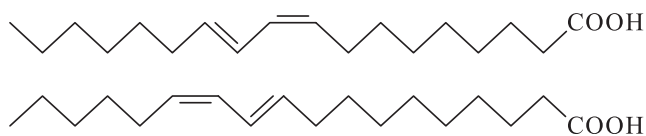
Fig. 1. Structures of cis-9, trans-11 and trans-10, cis-12 CLA isomers.

surfactant monomers through the membrane to an unacceptable level over time. If the monomers within the micelles can be cross-linked, the new nanoparticles will be stable and loss of monomers across the membrane will not occur [15]. Due to the ease by which the conjugated double bonds of CLA can be polymerized across surfactant monomers, several nanomaterials potentially could be synthesized from this surfactant that have the potential to be used in various applications, including in several applications for treating water or wastewater.

In this study, CLA micelles were cross-linked upon exposure to heat, and the resulting stearic acid (SA) nanoparticles were purified by repeated dialysis. Hence, this study reports on the stability and properties of the SA nanoparticles in water and provides further information on the properties of CLA in water. A further intent of this study was to inform us and others about the potential for using CLA to synthesize other cross-linked materials, as the carboxylic acid functional group is easy to further functionalize. Size distributions of the SA nanoparticles were investigated by dynamic light scattering (DLS). The stability of the SA nanoparticles was confirmed by dialysis and from equilibration studies in different solvents. The association of a cationic dye, methylene blue (MB), to the SA nanoparticles across dialysis membranes was examined.

2. Materials and methods

2.1. Materials

CLA Liquid (95%) was purchased from Auhai Biotech Co., Ltd (Qingdao, China), and most of the impurities were reported to be oleic acid (2.5%) and linoleic acid (1.4%). Potassium persulfate (KPS) was purchased from Sigma-Aldrich (USA) and was used as a thermal initiator for cross-linking CLA when in micellar form. Methylene blue (MB), purchased from Sigma-Aldrich (USA), was 0.05% wt. in water. Potassium hydroxide (KOH), hydrochloric acid (HCl), and hexane were all analytical reagent grade. Deionized water was used throughout. Cellulose dialysis membranes were purchased from Biosharp, China with a molecule weight cut-off of 12,000 to 14,000 Da, and a diameter of 36 mm.

2.2. Titration of CLA solution

In order to determine the pK_a of CLA, the titration method was used. CLA dissolved in water with KOH was titrated incrementally with 0.1 M HCl. The volume of titrant and pH were recorded at the point when each solution first appears to be cloudy.

2.3. Surface tension

The surface tension (γ) of CLA solutions were measured as a function of temperature from 25° to 80° C, and as a function of KOH concentration with a Du Noüy ring tensiometer. The CMC at each temperature was determined from a plot of γ *versus* log[CLA]. Data at each temperature were collected in triplicate and the average values are reported.

2.4. Cross-linking of CLA micelles

CLA liquid (0.112 g) was dissolved in 100 mL water containing KOH. KPS was added to the solution and the mixture was sparged with

N_2 for 30 min. After sparging, the solution was heated to 80 °C for 10 h to cross-link the micelles [13]. A Cary 300 Bio UV–Visible spectrophotometer was used to monitor loss of absorbance due to the decreasing number of double bonds over time, as the conjugated double bonds absorb UV light with a peak absorbance at 233–234 nm. Dynamic light scattering (DLS) measurements of the CLA micelles and of the resulting cross-linked product were made with a Malvern Zetasizer Nano series instrument.

2.5. Dialysis of CLA and cross-linked SA nanoparticles

After cross-linking the micellar CLA, any residual non-cross-linked monomers within the nanoparticles or in the aqueous phase needed to be removed. Previous references have not reported on the removal of residual monomers [13]. By removing non-cross-linked monomers by repeated dialysis, the stability of the SA nanoparticles also was tested. To purify the SA nanoparticles, they were dialyzed 3 to 5 times until the monomer concentration in the dialysate was below the detection limit.

To compare the loss of monomers from micellar CLA solutions and cross-linked SA nanoparticles dispersions, 25 mL aliquots of cross-linked and non-cross-linked material were placed in dialysis membranes and equilibrated with a 125 mL external solution of KOH or pure water. The concentration of residual CLA monomers outside each dialysis membrane was evaluated by measuring UV light adsorbance, which indicates the presence of residual double bonds, and by measuring total organic carbon (TOC, with a TOC analyzer from Shimazu, Japan) which would indicate both unreacted CLA, and any monomeric material that had lost its π-bonds.

2.6. The distribution of CLA and SA nanoparticles in water and hexane

Previous studies [13,14] generally confirmed that cross-linking of CLA monomers occurred within the micelles by UV–Vis or IR spectroscopy measurements, as both methods can indicate the loss of the conjugated double bonds upon reaction. Loss of double bonds however does not confirm cross-linking has occurred, because oxidation and the formation of oligomers might also cause loss [24,25]. Hence, other methods are required to confirm cross-linking has occurred to a sufficient degree such that the resulting nanoparticle aggregates are stable in solution. The potassium salt of CLA forms micelles in water, but also forms reverse micelles (if no water is present) or water-in-oil emulsions (if water is present) in nonpolar solvents. However, sufficiently cross-linked nanoparticles will always retain a hydrocarbon core, and always possess a polar interface with the continuous phase. As a result, within a two-phase oil and water system, the cross-linked material should remain in the water phase upon mixing, and should not form inverted vesicles in the nonpolar oil layer. Hence, hexane and water layers were used to compare the phase distribution properties of non-cross-linked CLA and cross-linked SA nanoparticles. To this end, 2 mL hexane was layered onto 5 mL aqueous solutions containing either non-cross-linked CLA (in 0.1 M KOH), or cross-linked SA nanoparticles immediately after the thermal cross-linking process (before dialysis, so before removal of non-cross-linked monomers), or SA nanoparticles after dialysis. Hexane and water without any additives was used as a control. These 4 samples were shaken by hand for 30 s, and then allowed to stand for 24 h. The concentration of CLA in each water phase was measured at 0.5 and 24 h.

2.7. Adsorption of methylene blue onto the SA nanoparticles across dialysis membranes

Methylene blue (MB) was used as a representative organic cation (chemical probe) because its highly visible blue color makes it easy to see in solution. Across dialysis membranes (the membranes were saturated in MB solution before experiments), external solutions of 10 to 40 mg/L MB (80 mL, pH 7.0 or 11.2) were equilibrated with internal