Colloids and Surfaces A: Physicochem. Eng. Aspects 457 (2014) 345–353

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Rheological properties of the gels of biological surfactant sodium deoxycholate/amino acids/halide salts systems

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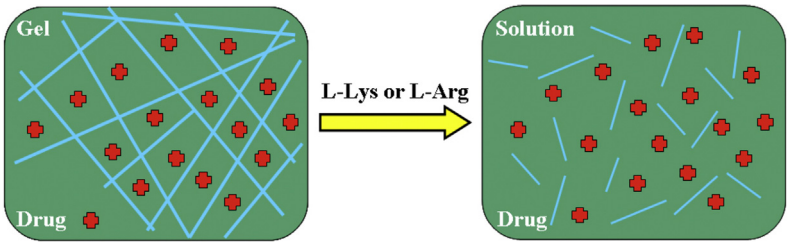
HIGHLIGHTS

- We used biological surfactant sodium deoxycholate to prepare hydrogels.
- NaCl and NaBr can strengthen the network structure of hydrogels.
- L-Lysine and L-Argamino acids can destroy the network structure of the hydrogels.
- These hydrogels have potential applications in the field of as smart materials for drug controlled release materials.

GRAPHICAL ABSTRACT

Among various applications, drug delivery is one of the significant properties of hydrogels and this interesting modification of the NaDC hydrogels may enhance its applications in biomedicine for tunable drug delivery. The drugs which are embedded into the network structure of hydrogels could be released to the nidus positions when the network structures are destroyed encountering L-Lys or L-Arg.



ARTICLE INFO

Article history:
Received 15 January 2014
Received in revised form 28 May 2014
Accepted 4 June 2014
Available online 12 June 2014

Keywords:
Hydrogels
Sodium deoxycholate
Amino acid
Rheological properties
Hydrogen bonds

ABSTRACT

Rheological properties of biological surfactant sodium deoxycholate (NaDC) in the presence of two amino acids (L-Lys and L-Arg) and two halide salts (NaCl and NaBr) have been investigated systematically at 20 °C and pH = 6.864. The gel-to-sol transition behavior induced by the addition of amino acids can be observed. It is found that the viscoelasticity of the hydrogels of 50 mmol L^{-1} NaDC decreased when L-Lysine (L-Lys) or L-Arginine (L-Arg) was added in the system. However, the addition of halide salts NaCl or NaBr in the above system resulted in an opposite trend. In view of these phenomena, a conclusion was given that L-Lys and L-Arg amino acids can destroy the network structure of the hydrogels while NaCl and NaBr can strengthen it. Moreover, it is found that the viscoelasticity of the L-Lys-containing hydrogel is higher than that of L-Arg-containing hydrogel at the same condition, on the other hand, the viscoelasticity of NaCl-containing hydrogel is higher than that of NaBr-containing hydrogel at the same concentration, indicating that NaCl performs better in strengthening the network structure of the hydrogels than NaBr. Furthermore, thixotropic experiments have also been done and revealed that the NaDC hydrogels prepared in this work possessed excellent thixotropic properties, which have potential applications in the field of as smart materials for drug controlled release materials.

1. Introduction

Supramolecular gels belong to a fascinating class of soft materials in which a large number of solvent molecules are immobilized by the network structure provided by the assembled gelator molecules [1] and they have shown large potentials in fields of

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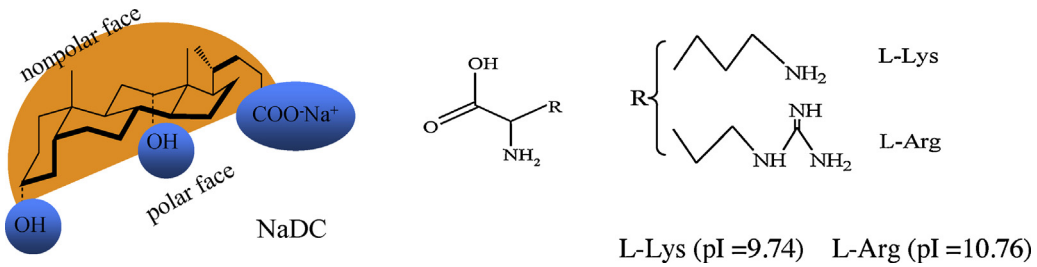
http://dx.doi.org/10.1016/j.colsurfa.2014.06.003
0927-7757/



Scheme 1. The structures of NaDC and amino acids.

drug delivery [2], 3D cells culture [3], biocatalysis [2], bioanalysis [4], tissue engineering [5], etc. Composed of three-dimensional, elastic networks and a liquid molecules in their interstitial spaces, gels possess many useful properties, such as forming hierarchical structures, flowing in response to a shear force [6], and exhibiting phase transitions upon other stimuli such as a change in temperature [7], variation of the pH value [7], enzymatic conversion [8], and irradiation of light [9]. These gelator molecules are generally based on small organic molecules [10]. Up to now, a variety of small organic molecules has been found to form low-molecular-weight gels [11,12], including amides, peptides, ureas, saccharides, nucleobases, molecules with long alkyl chains, steroid derivatives, etc.

Bile salts are important biological surfactants, which exist in the living bodies of vertebrates [13,14] and often act as solubilizing or emulsifying agents for absorption of dietary lipids [15], gallstone solubilizing agents in clinical medicine [16] and physiological surfactants in the digestion of fat and the excretion of excess cholesterol. Structurally, bile salts are an unusual class of amphiphiles: unlike typical surfactants containing a polar head and a nonpolar tail, all of them possess a rigid steroid backbone with polar hydroxyl groups on the concave α-face and methyl groups on the convex β-face [17]. This arrangement creates unique physiochemical properties for such a class of molecules, being different from those of conventional surfactants with a linear hydrocarbon chain [15]. It is worth mentioning that bile salts can interact with the ubiquitous proteins, whatever in vitro and in vivo of body [18]. Consequently, interaction between bile salts and proteins is a subject of intensive research [19,20]. Amino acids are considered to be the component units of the complex proteins. Thus, there is currently a considerable amount of interest in the interaction between amino acids and surfactant in aqueous solutions [15]. Especially, the gels formed by bile salts and amino acids can may act as drug carriers and be used in bioengineering and drug delivery systems.

Rheological analysis of hydrogels is meaningful, especially in the pharmaceutical applications, since its mucoadhesive performance is closely related to the rheological properties [21]. The viscoelastic properties of the hydrogels of bile systems are considered to be of great importance for understanding the vital biological functions and practical applications [22]. Hence, the rheological properties of such systems should be explored in more detail. In this paper, the gels of NaDC in the presence of inorganic salts (NaCl or NaBr) were prepared and they exhibited phase transition behavior from macroscopic gel to solution in response to two kinds of amino acids (L-Lysine (L-Lys) or L-Arginine (L-Arg)). The properties of our systems have been characterized by phase behavior observation, differential scanning calorimetry (DSC) and rheological measurements. The roles of the hydrophobic chain, the chiral rigid steroid center, the structures of amino acids and the hydrogen bonds in the formation of hydrogels are clearly described. These hydrogels can be used for the controlled release of drugs entrapped within the gel network in response to the presence of specific amino acids.

2. Experimental

2.1. Chemicals and materials

Analytical reagent sodium deoxycholate (NaDC, Sinopharm Chemical Reagent Co.) was purified as described elsewhere [15]. Biochemical reagent grade L-Lysine (L-Lys) and L-Arginine (L-Arg) and analytical reagent grade sodium chloride (NaCl) and sodium bromide (NaBr) were purchased from Sinopharm Chemical Reagent Co. and used without further purification. The structures of NaDC, amino acids and their isoelectric point (pI) are shown in Scheme 1. All solutions were prepared in sodium phosphate buffer with pH = 6.864, which was prepared by using 0.025 mol L^{-1} KH_2PO_4 and 0.025 mol L^{-1} Na_2HPO_4 mixed standard buffer solution (20 °C, pH = 6.864) (A.R. Shanghai Reagent Co.) in appropriate amounts at 20 °C. Water used in the experiments was triply distilled by a quartz water purification system. It's with a conductivity was lower than 1.8 μS cm^{-1} as measured by a DDSJ-308A type conductivity instrument in our laboratory.

2.2. Sample preparation

Stock solutions were prepared by dissolving appropriate amounts of NaDC, amino acids and NaX (X = Cl or Br) in sodium phosphate buffer (pH = 6.864), respectively. The stock solutions were placed for several days at room temperature until all samples solids dissolved. A series of sample solutions was then prepared by mixing different amounts of the stock solutions to obtain desired concentrations until the final volume of each sample reached 4 mL. The solutions were stirred mildly at room temperature until all the components evenly mixed. Then the samples were equilibrated at 20.0 ± 0.1 °C for at least 4 weeks at least prior to the phase behavior was inspected study.

2.3. DSC measurements

DSC measurements were performed by a DSC Q10 V9.7 Build 291 in a DSC standard cell FC. An empty aluminum pan was used as a reference. The gelled samples were equilibrated at 20.0 ± 0.1 °C for 10 min and then heated to 50 °C at a heating rate of 3 °C min^{-1}.

2.4. Rheology

The rheological measurements were carried out on a HAAKE RS75 Rheometer (Germany) with a cone–plate system (Ti, diameter, 35 mm; cone angle, 1°). Rate control mode, CR, was chosen in the steady-state shearing experiment, the range of shear rates was from 0.2 s^{-1} to 1000 s^{-1}. The stress sweep was carried out with the stress range from 0.01 Pa to 20.00 Pa at a fixed frequency of 1.00 Hz. Then the oscillatory frequency sweep measurements were carried out at a frequency between 0.01 Hz and 10.00 Hz in the oscillation mode, OSC. Thixotropic experiments were conducted to examine the recovery behavior of hydrogels after deformation. The elastic modulus (G') and viscous modulus (G'') are recorded as a function