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Colloids based on gold nanoparticles dispersed in castor oil: Synthesis parameters and the effect of the free fatty acid content

Colloïdes à base de nanoparticules d'or dispersées dans de l'huile de ricin : paramètres de synthèse et l'effet de la teneur en acide gras libre

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ABSTRACT

Herein, we present our results related to the synthesis of colloidal solutions of gold nanoparticles (AuNPs) dispersed in castor oil. These colloids were prepared via a wet chemistry process by mixing specific amounts of castor oil, ethanol, and aqueous solutions of tetrachloroauric(III) acid and sodium hydroxide. The size and shape of the AuNPs obtained could be modulated by the amount of gold source added and the Au/OH^- molar ratio used. In this study, we observed that the free fatty acid content in the reaction medium was an important parameter to be considered in the syntheses of the colloidal solutions and the respective form and shape of the AuNPs produced. Thus, we evaluated the effect of oil acidity by adding different amounts of myristic acid (MA) in the reaction medium. The colloids were characterized by UV–vis spectroscopy, and the size and shape of the AuNPs produced were characterized by transmission electron microscopy (TEM).

1. Introduction

The singular properties of colloidal systems containing gold nanoparticles (AuNPs) have been recognized and studied for centuries [1]. Nevertheless, several efforts are still underway to develop new nanostructured materials based on AuNPs with outstanding and unique properties. Thus, new methods for colloidal gold particle production continue to be developed and published in specialized literature [2–4].

Most of the methods employed for AuNP production are based on wet chemistry, using water as a solvent [1,5–8]. However, organic solvents, such as toluene [9], ionic liquids [10,11], and vegetable oils [12–24], are also used. This last solvent type (vegetable oils) in particular is now considered a promising vehicle for preparing organic–inorganic nanostructured materials with attractive biomedical applications [25,26]. Most of this potential arises from the biocompatibility and liposolubility that these materials can potentially display [27,28], allowing for new alternatives for nanoparticle transport [14] and assimilation into living organisms. Among the vegetable oils used to prepare and stabilize colloidal nanoparticles, castor oil has received particular attention [19,24].

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It is worth mentioning that castor oil is classified by the Food and Drug Administration (FDA) as a safe and effective stimulant laxative [29] and can be used to enhance the transdermal penetration of drugs and chemicals; furthermore, castor oil presents suppressive effects against tumorous cancers [28–30].

The techniques used for the preparation of colloidal solutions based on metal nanoparticles dispersed in vegetable oils include sputtering deposition [19], laser ablation [20], and molecular precursor reduction [23,24]. Recently, we developed a very simple method for AuNP preparation [24] using a two-phase synthesis approach (water–castor oil), employing $HAuCl_4$ as a gold source in the presence of a base (KOH). This strategy leads to very stable colloids of AuNPs dispersed in castor oil that display very intense colors and non-linear optical properties [31,32]. With this synthesis method, it is possible to obtain colloidal solutions of AuNPs with only castor oil as the organic solvent. Conventional vegetable oils, such as soybean, cotton or sunflower oils cannot be used to prepare stable colloids. Thus, the peculiar properties of castor oil must be related to the singular molecular composition of the oil [33–37], and for that reason, castor oil has found use in a number of industrial applications, including the production of coatings, plastics, and cosmetics and medicinal applications [38,39]. Castor oil is a mixture of triglycerides formed predominantly (approximately 90%) by the ester form of the ricinoleic acid, (9*Z*,12*R*)-12-hydroxy-9-octadecenoic acid (Fig. 1). The presence of the hydroxyl group in the fatty acid chain, which is not present in conventional vegetable oils, is the main reason for the unusual proprieties of this vegetable oil [34,37]. For example, castor oil is completely soluble in alcohols and displays a viscosity that is up to seven times greater than the viscosities of other vegetable oils [40]. It was also recently observed that castor oil presents strong non-local non-linear optical properties [31,41,42].

In a previous study, we developed three synthesis methods using castor oil as a AuNP dispersant [24,43]. Those methods using KOH and sodium citrate to induce AuNP formation were observed to be the most favorable for obtaining AuNPs with reasonably uniform size and shape. These results prompted us to acquire more details regarding the synthesis parameters, particularly in the case in which KOH was used to induce nanoparticle formation. Parameters such as the amount of the gold source, the Au/OH^- molar ratio, and the oil acidity were systematically varied to verify their effects on the features of the AuNPs produced.

2. Experimental

2.1. Materials

Castor oil, tetrachloroauric(III) acid ($HAuCl_4 \cdot 3H_2O$), and myristic acid were obtained from Acros Organics (Morris Plains, NJ, USA) and used as received. Potassium hydroxide (KOH), anhydrous magnesium sulfate ($MgSO_4$), and solvents employed for stability tests were obtained from Vetec (São Paulo, SP, Brazil) and used as received. Absolute ethanol was obtained from DINÂMICA (São Paulo, SP, Brazil). All aqueous solutions were degassed and prepared with distilled water. The free fatty acid content of the castor oil was equivalent to 1.2% (determined according to the AOCS official method Ca 5a-40).

2.2. Synthesis of the colloids

Colloids were prepared using a method similar to that previously developed in our research group [24]. Depending on the synthesis parameters applied, different sizes and shapes of AuNPs can be obtained. A typical procedure adopted for all syntheses was performed as follows. In a two-necked, 100-mL, round-bottom flask equipped with a magnetic bar, a septum, and a reflux condenser, a mixture of castor oil (10 mL, net or mixed with myristic acid), ethanol (10.0 mL), and an aqueous solution of $HAuCl_4 \cdot 3H_2O$ (0.025 M, 2.0 mL) was prepared. The mixture was heated to 50 °C, and an aqueous solution of KOH (0.10 M, 1.0 mL) was then added with a syringe through the septum under vigorous stirring. The bath temperature was then immediately set to 80 °C. The color of the mixture soon changed to a deep red (or blue if the appropriate amount of myristic acid was added to the reaction medium). After 24 h of stirring, the mixture was cooled to room temperature, and the organic phase was recuperated, washed with water (10 mL), centrifuged to remove the excess water (3000 rpm), and dried under high vacuum for at least 7 h.

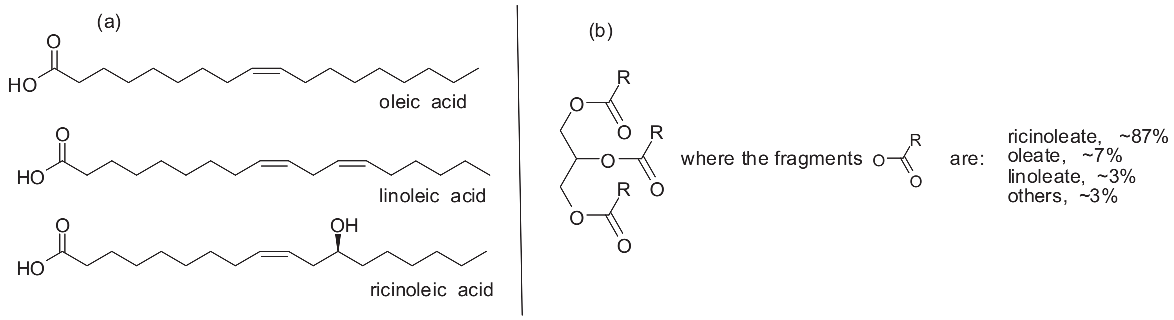

Fig. 1. General molecular structure of (a) oleic, linoleic, and ricinoleic acids, depicted to illustrate the typical chemical structure of fatty acids, and (b) general chemical structure of a triacylglyceride and the most important fragments of carboxylic acids derivatives present in castor oil.