Research Paper

Volume : 4 | Issue : 6 | June 2015 • ISSN No 2277 - 8179

Inverse Microemulsion Route for Synthesizing Uniformly-Distributed Monodisperse Calcium Phosphate Bioactive Nanomaterials.

Nanoscience

KEYWORDS : Microemulsion, mixed-surfactants, calcium phosphate, nanocrystals

Dr. Vaishali Singh

USBAS, Guru Gobind Singh Indraprastha University, Sector -16C, Dwarka, New Delhi-110078 (India)

ABSTRACT

Inverse microemulsion route is adopted to synthesize nanosized calcium phosphate particles. The technique uses a mixed surfactant system of Tween20 and Aliquat336 in order to obtain novel morphologies of the calcium phosphate nanocrystals. The nanopowders are extensively characterized by Fourier Transform Infra Red Spectroscopy, X- ray Diffraction, Scanning Electron Microscopy, and Transmission Electron Microscopy and are found to possess high crystallinity. TEM and SEM micrographs reveal the size and shape of the formed nanopowders. Lath shaped and spherical particles (average diameter 129nm) were obtained. Nature of surfactant and the precursor concentration play a significant role on the shape and morphology.

Introduction

Calcium phosphate is a material of immense biological application due to its structural and chemical resemblance to natural bone. It is found to exist in several forms like hydroxyapetite (HAP), Tricalcium phosphate (TCP) and Octacalcium phosphate (OCP), monetite (DCPA) and brushite (DCPD) [1] among which, brushite has been proposed as an intermediate in bone mineralization and enamel dissolution. As a result, calcium phosphates are extensively used biomaterials in bone substitution and maxillofacial reconstruction, in orthopaedics and in dental applications like tooth replacement [2].

In recent years, emergence of nanoscience and technology has made possible the control of matter with dimensions of roughly 1-100nm, which gives rise to unique and enhanced properties of materials. One of the most important features of the nanomaterials is their increased surface area to volume ratio that makes them highly suitable for several applications. Owing to its wide applicability lots of research interest has aroused worldwide in investigating the reaction conditions for tailor-making its various forms [2, 3].

The general approach used for nanomaterial synthesis is broadly either the 'Top-down' approach or the 'Bottom-up' approach. Chemical methods involving the building up of nanoparticles from molecular-dimensions constitute the "Bottom-up" approach. Chemical methods have been widely used to produce nanostructured materials due to their straightforward nature and potential to produce large quantities of the final product. The common chemical methods are chemical co-precipitation, sol-gel process, hydrothermal process and microemulsion method. The microemulsion process has emerged as one of the best methods to obtain uniform-size distribution and a monodisperse sample.

This paper first describes in detail the mechanism of reverse microemulsion, followed by the synthesis of calcium phosphate nanoparticles by this route using a soft template of mixed surfactants followed by the characterization of the product formed by the FTIR, XRD, SEM and TEM.

Microemulsion

The term microemulsion was first coined by Hoar and Schulman [4], who described it as a transparent system which formed spontaneously upon the mixing of the oil and water with a relatively large amount of an ionic surfactant, together with a co-surfactant. The surfactant in Schulman's study was cetyltrimethylammonium bromide (CTAB) which is still being used frequently. Although a variety of surfactants belonging to various categories like ionic, non-ionic, zwitter-ionic or Gemini are being used nowadays giving rise to a wide range of morphologies and size control.

The term surfactant implies surface active agents, these molecules are amphiphilic in nature, they are composed of a water-loving and an oil-loving moiety. The water loving end is usually referred to as the polar head and the long hydrocarbon chain or the hydrophobic part, as the tail.

When such a molecule is added to an oil- water mixture, they first tend to accumulate at the interface and then orient themselves in a way that leads to minimum hydrophilic-hydrophobic interactions, as a result hydrophobic chains tend to expel contact with water. This driving force leads to a preferred arrangement of surfactants called the self-assembly. Thus, if surfactant is added to an oil in water system, the hydrophobic tails will be directed towards the oil and polar groups in water. This leads to the self- assembly of these molecules in the form of micelles. Micelles may take up various shapes and sizes depending upon several factors, the most important one being the critical packing parameter (CPP) of the surfactant, which is expressed as:

$P = v/ al$

Where, different P values yield various shapes of surfactant self-assembly, explained by the Fontell Scheme [5].

The preferred geometry in which the surfactant molecules self assembles directs the shape and size of the nanomaterial being synthesised. When the critical packing parameter is greater than 1, reverse micelle formation takes place. They are characterized by the w_o the molar ratio of water to surfactant, s:

$$wo = [H_2O] / [S] \quad - (1)$$

To establish the relationship between wo and the micellar radius RM we first consider the micellar molar volume, VM given by:

$$VM = 4 \pi RM^{3/3 = n}sVs + nw\ Vw \quad - (2)$$

Where, ns and nw are the moles of surfactant and water per micelle, respectively and Vw is the volume of water in the micelle [6]. Assuming that the surface area of a micelle, ∑M, is determined solely by the surfactant, then

$$\sum M = 4\pi\ RM^{2 = n}s\ \sum_s \quad - (3)$$

Where, $\sum_s$ is the molar interfacial area at the surfactant-oil boundary. Since the volume in this model is fixed, thus

$$wo = [H_2O] / [S] = n_w\ n_s \quad - (4)$$

combining equations (2) – (4) gives:

$RM = 3\ V_s/ \sum_s + 3\ V_w\ wo/ \sum_s$ Experimentally, RM has been shown to vary linearly with water content in reverse micellar

systems above a critical wo of 10, below which V_s, V_w and $\sum_s$ also increase with increasing wo. These findings were carried out with AOT and CTAB as the surfactants [7]. As such, the size of the water pool at the reverse micelle core can be carefully controlled by adjusting the $[H_2O]/[S]$ ratio, provided wo ≥ 10.However, controlling the size reverse micelles does not address the issue of micelle formation. As a four- component mixture of oil-water-surfactant–co-surfactant, the phase equilibria of reverse micelle systems are inherently complex [8]. The phase relationship of such systems are depicted with Gibbs triangles [9].

Reaction Dynamics in Reverse Micelles

Reverse Micelles or W/O microemulsions are mostly transparent, isotropic liquid with nano-sized water droplets dispersed in the continuous oil phase and stabilized by surfactant molecules at the water-oil interface.

The microenvironment created by surfactant- covered water pools not only act as microreactors for reactions but also inhibit the aggregation of particles due to the formation of an adsorbed layer of surfactants on the particle surface.

The small size of reverse micelles subjects them to continuous Brownian movement, even at room temperature, as a result particles obtained by this route are very fine, monodisperse, morphologically controlled and highly crystalline as compared to normal microemulsion [10, 11].

A schematic illustration of microemulsion mixing, that allows the interchange of reactants along the droplets via a transient short-lived dimer is given as under:

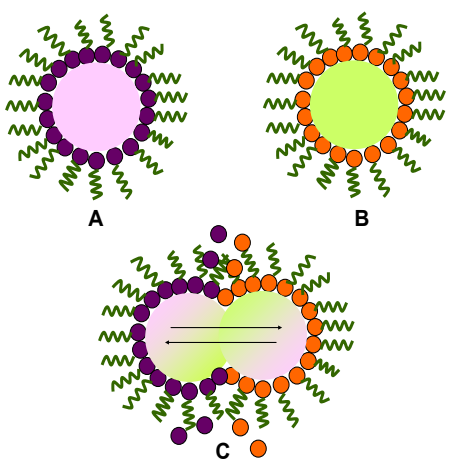

Figure 1: Schematic representation of a collision between two reverse micelles with dissimilar cores. The micelles form a short-lived dimer, as some surfactants molecules are released into the oil phase and the contents of the micellar cores are exchanged.

The resultant size distribution of the particles formed is a complex function of various factors like nucleation and growth rate and Ostwald ripening. Reverse micelle holds a great potential for being the preferred route for synthesis of fine nanoparticles.

Synthesis of calcium phosphate nanoparticles by reverse microemulsion using a mixed surfactant system

Three inverse microemulsions namely I_1, I_2 and I_3 were setup using a system of mixed surfactants- Tween20 a nonionic surfactant and Aliquat336 a cationic surfactant.

Two types of reverse microemulsions, one quaternary Q1, Q2, Q3 containing Tween20 (19.512wt%), Kerosene (53.659wt%) , Isopentanol (19.512wt%) , water (7.32wt%) and other pentanary- P_1, P_2, P_3 containing Tween20 (17.0732wt%), Aliquat336 (2.439wt%), Kerosene (53.659wt%), Isopentanol (19.512wt%), water (7.32wt%) were prepared for the three systems obtained on mixing Q and P.

Water phase in quaternary and pentanary reverse microemulsions was the aqueous solution of $Ca(NO_3)_2.4H_2O$ [0.2, 0.15 and 0.10M] and aqueous solutions of $(NH_4)_2HPO_4$ [0.12, 0.09 and 0.06 M] respectively. The pH for the reverse microemulsions were found to be in between 4-5 and 6-7, respectively. The pH for the final reaction mixture was found to be between 4-5.

Now the reverse microemulsions P were added slowly to reverse microemulsions Q with constant stirring on magnetic stirrer for 5 min. The reaction mixture was then aged for 4 days at room temperature. After 4 days, centrifugation was done and white precipitates were collected, washed several times with methanol and then dried in the hot air oven at 80°C for nearly 5 hours.

Characterization:

FTIR Spectra

Fourier Transform Infrared Spectroscopic measurements were taken on Shimadzu Japan (FTIR-8700) Spectrophotometer. Samples of prepared nanoparticles were mixed with KBr, homogenized and converted into pellets under a pressure of 8 ton and the spectrum was recorded. The spectra matched well with standard spectra observed for bulk calcium phosphate [12, 13].

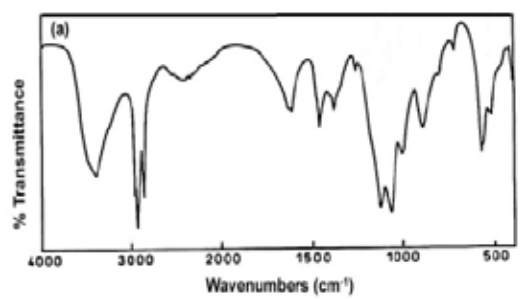

Figure 2: The FTIR spectrum of CP nanoparticles obtained from Tween 20/ Aliquat 336 based mixed surfactant system [0.2M $Ca(NO_3)_2$ and 0.12M $(NH_4)_2HPO_4$].

XRD results

The XRD results are in good agreement with the ICDD standard file (02-0085). The XRD pattern gave a series of diffraction broad peaks assigned to mainly brushite phase. The peak around 12°, 21°, 23.9°, 29.3°, 30.5°, 34.5°, 36.2° corresponding to Miller indices of (020) (021) (040) (041) (221) (202) (022) are observed in the XRD diffractograms that confirms the formation of brushite.

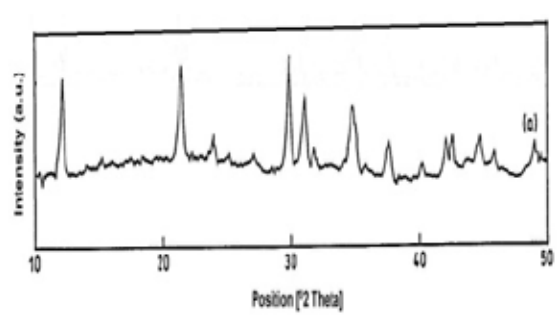

Figure 3: The XRD data of CP nanoparticles with Tween 20/ Aliquat 336 based mixed surfactant system.

Morphological and Particle size distribution

TEM images obtained for synthesized particles show the presence of two shaped – lath shaped as well as spherical particles

Volume - 4 | Issue - 6 | June 2015 - ISSN No 2277 - 8179

having an average diameter of 129nm. Figure 4 about here.

SEM images show fine lath shaped nanoparticles having smooth surface with well-defined boundaries. These boundaries become more well-defined as the precursor concentration is decreased. Thus, nature of the surfactant plays a significant role in assigning the morphology to calcium phosphate nanoparticles. Studies have shown that single surfactant, Tween 20 leads to a coarse network whereas when mixed with Aliquat 336, fine network is formed. Figure 5 about here.

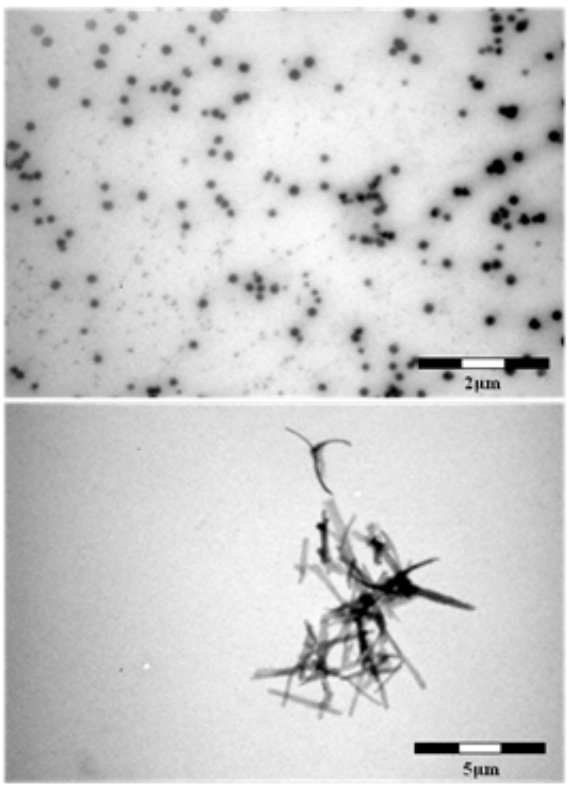

Figure 4: TEM images of CP nanoparticles with Tween 20/ Aliquat 336 based mixed surfactant system. [0.2M Ca(NO3)2 and 0.12M (NH4)2HPO4].

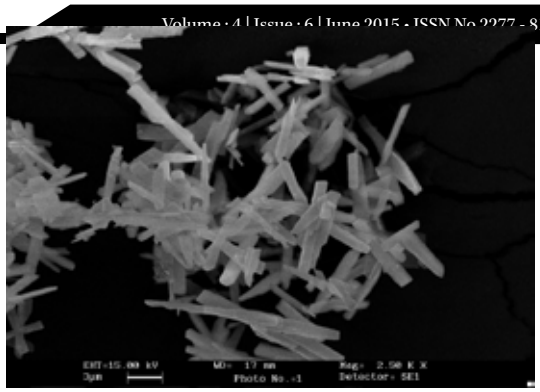

Figure 5: SEM image of CP nanoparticles with Tween 20/ Aliquat 336 based mixed surfactant system. [0.2M Ca(NO3)2 and 0.12M $(NH_4)_2HPO_4$].

REFERENCE

Tortet, L.; Gavarri, J. R. ; Nihoul, G. ; | Dianoux, A. J. (1997) . Study of | protonic mobility in CaHPO4.2H2O | (brushite) and CaHPO4 (monetite) by | infrared-spectroscopy and neutron- | scattering. J. Solid State Chem. | 132, 6. doi:10.1006/jssc.1997.7383 | Rao, C. N. R.; Müller, A. ; Cheetham, | A.K. (2004) . The Chemistry of | Nanomaterials. Nanomaterials – An | Introduction Wiley-VCH: Weinheim. | doi: 10.1002/352760247X.ch1 | Dubok, V. A. (2000) . Biocreamics: | Yesterday, today, and tomorrow. | Powder Metall. Met. Ceram. N7-8, | 69. doi: 10.1023/A:1026617607548 | Danielsson, I.; Lindman, B. (1981) . The | definition of microemulsion. Colloids | Surf. 3, 391. doi: 10.1016/0166- | 6622(81)80064-9 | Holmberg, K.; Jönsson, B.; Kronberg, B, | Lindman, B. (2004) . Surfactants and | Polymers in aqueous solution (2nd | ed.) England, MA: John Wiley & | Sons, Ltd. | Liveri, V. T. (2002) . Reversed micelles | as nanometer-size solvent media. In | Nano-Surface Chemistry; Dekker: | New York, 473 | Cheng, G. X.; Shen, F; Yang, L. F.; Ma, | L. R.; Tang, Y.; Yao, K. D.; Sun, P. | C. (1998) . On properties and | structure of the AOT–water– | isooctane reverse micellar | microreactor for nanoparticles. | Mater. Chem. Phys. 1998, 56, 97. | doi:http://dx.doi.org/10.1016/S0254- | 0584(98)00132-1 | D'Aprano, D;Lizzio, A.; Liveri, V. T. | (1987) . Enthalpies of Solution and | Volumes of Water in Reversed AOT | Micelles. J. Phys Chem. 91, 4749. doi: | 10.1021/j100326a038 | Kunieda, H.; Shinoda, K. (1979) . Solution | behavior of aerosol ot/water/oil system. | J. Colloid Interface Sci, 70, 577. | doi: 10.1016/0021-9797(79)90065-1 | Pileni, M. P.; Fendler, J. H. (1998) . | Nanoparticles and Nanostructured | Films. Wiley-VCH, Weinheim | Paul, B. K.; Moulik, S. P. (1997) . | Microemulsions: An overview. J. | Dispers. Sci. Technol. 18, 301. doi: | 10.1080/01932699708943740. | Gadaleta, S. J.; Paschalis, E. P.; Betts, | F.; Mendelsohn, R.; Boskey, A. L. | (1996) . Fourier transform infrared | spectroscopy of the solution- | mediated conversion of | amorphous calcium phosphate to | hydroxyapatite: new correlations | between X-ray diffraction and | infrared data. Calcify, Tissue Int, 59, 9. | doi: 10.1007/BF02509540 | Pleshko, N.; Boskey, A.; Mendelsohn, R. | (1991) . Novel infrared spectroscopic | method for the determination of | crystallinity of hydroxyapatite | minerals. Biophys J. 60, 786. doi: | 10.1016/S0006-3495(91)82113-0