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RESEARCH PAPER

Entrapment–D-(+)-Glucose Water Nanodroplet: Synthesis and Dynamic Light Scattering

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ABSTRACT

In the present research, the D-(+)-Glucose–confined water nanodroplets with mean size in the range of 6-11 nm were synthesized at D-(+)-Glucose different concentrations by AOT reverse micelles (RMs) method as a function of mass fraction of droplet (MFD) at the constant water-to-surfactant molar ratio (W=40). The dynamic light scattering of the nano-sized water droplets containing the D-(+)-Glucose monosaccharide showed that interaction between the nanometer-sized AOT droplets changed from attractive to repulsive as the hydrophilic D-(+)-Glucose concentration increased as a function of MFD. The hydrodynamic diameter of water droplets increased as concentration of D-(+)-Glucose monosaccharide decreased in the water-in-oil AOT microemulsion.

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INTRODUCTION

In water-in-oil AOT microemulsions (ME) that are clear and thermodynamically stable, water droplets in the nanometer range (1–50 nm) are formed and stabilized by the AOT anionic surfactant monolayer in the bulk non-polar solvent, which can solubilize water-soluble bio-molecules such as enzymes, DNA, proteins, amino acids [1-3]. The AOT nano-sized droplets are formed at the specific mass ratios of H_2O, AOT surfactant and hydrophobic solvent [1-3]. Efforts to study the inverse microemulsions has encouraged as they are used in a range of applications such as oil recovery, drug delivery, enzymology, nano-particle synthesis, and as nano-scale reactors for aqueous reactants and framework for nanometer-size hydrogel particles [4-8]. Reverse microemulsion polymerizations was developed in the last two decades to prepare thermodynamically stable latexes in the nanometer-sized range (<50 nm) [9]. In literatures, the aqueous solution of D-(+)-Glucose mono-saccharine has been reported [10-11]. Previous studies in fields of water-in-oil AOT RMs comprising additives have only been limited to research about their dynamical behavior at the different water-to-surfactant molar ratios (W), oil, temperature, pH, etc [12] but an neglected area in the field of dynamic of AOT inverse microemulsions containing bio-molecules is study of the additive-loaded water-in-oil reverse micelles at the different additive concentrations at the constant water content (W=40). Therefore, in present research, the dynamic of nano-sized water droplets containing D-(+)-Glucose was studied in the water/AOT/decane RMs by changing the D-(+)-Glucose concentration at the fixed water to AOT ratio molar (W=40) as a function of MFD by the DLS technique. The behavior of the

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water-in-oil microemulsion system containing the hydrophilic additive depends on the interaction between the water droplets and the additive or surfactant molecules that leads to non-adsorbing or adsorbing additives in the core of water nano-droplets or H_2O/surfactant interface, respectively [13-16].

It is important to mention that Glucose is a sugar with the molecular formula $C_6H_{12}O_6$ (Fig.1). Glucose is made during photosynthesis from carbon dioxide and water by using energy from sunlight. The reverse of the photosynthesis reaction, which releases this energy, is a very important source of power for cellular respiration .The molecular structure of D-(+)-Glucose has been shown in Fig.1. In the literature, the transdermal delivery of flux of glucose by water-in-oil microemulsion as one of the best delivery methods has been reported [27].

MATERIALS AND METHODS

The dioctyl sodium sulfosuccinate , AOT (Sigma–Aldrich, purity >99%), Decane oil and D-(+)-Glucose from Sigma–Aldrich, were used as received.

Preparation of d-(+)-glucose-loaded water nanodroplets

To prepare the entrapment–D-(+)-Glucose nanodroplet, at the first, weighed powder of D-(+)-Glucose monosaccharide was dissolved in the distilled water in terms of the certain concentration at room temperature . The mass ratio of D-(+)-Glucose to H_2O, was defined as concentration of the D-(+)-Glucose in the Aerosol-OT RMs [28]. The water-in-oil AOT inverse micro emulsions were prepared by mixing the appropriate mass values of the decane oil , deionized water containing the different D-(+)-Glucose concentrations and AOT anionic surfactant following the constant H_2O-to-AOT molar ratio (W=40) and then, the system was diluted with decane following the defined MFD, where MFD= $(M_{Nanodroplet})/(M_{Total}))$ [23,28] in the AOT RMs at room temperature (RT).

Characterization

The autocorrelation function of AOT nano-droplets was achieved by using dynamic light scattering technique.

The size of water droplets in nanometer scale confirmed using a Zetasizer Nano ZS (Malvern Instruments, Germany) equipped with a He−Ne laser source (633 nm) with vertically polarized light.

RESULTS AND DISCUSSION

Theory of Dynamic Light Scattering

Dynamic Light Scattering (DLS) is a useful technique for the size distribution characterization of nano-sized particles by modulation analysis the time autocorrelation function of the scattered light intensity from a laser light that passes through a colloidal solution. The DLS based on the motion and diffusive behavior of droplets in the colloidal solution according to their size and viscosity of continuous phase. The normalized intensity–intensity autocorrelation function of the scattered light as function time, $g^2(q,\tau)$ for a given delay time τ is given by [17-19 ,28].

$$g^2(q,\tau) = \frac{\langle I(q,t)I(q,t+\tau)\rangle}{\langle I(q,t)\rangle^2} \quad (1)$$

Where I (q, t) and I (q,t + τ) are the scattered light intensities at times t and t + τ, respectively, and the braces denote to averaging over t.

The autocorrelation function, $g^2(q, \tau)$ is related

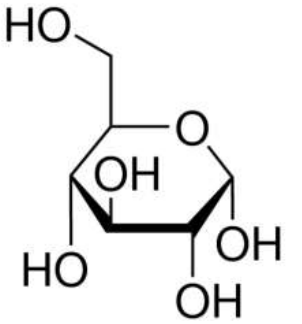

Fig. 1. Chemical structure of D-(+)-Glucose

to the normalized autocorrelation function of the electric field $g^1(q,\tau)$ by the Siegert relation [17-19].

$$g^2(q,\tau) = 1 + \beta\left|\exp(-Dq^2)\right|^2 \qquad (2)$$

Where β is the experimental coherence factor [17-19] and q is magnitude of the scattering light vector. Finally, the diffusion coefficient can be interpreted as the hydrodynamic diameter r_h by the Stokes-Einstein relation [17-19]:

$$r_h = \frac{K_B T}{6\eta\pi D} \qquad (3)$$

Where k is Boltzmann's constant, T the temperature in K, and Γ is the viscosity of continues phase. In this work to study of the size distribution characterization and diffusion of water droplets containing monosaccharide of D-(+)-Glucose in the AOT RMs.

In this investigation, the dynamic of nano-sized water droplets containing of D-(+)-Glucose in water-in-oil microemulsion was studied. The water droplets were formed via mixing the AOT, decane oil and water containing the different D-(+)-Glucose concentrations (0.001,0.00025 and 0.0000625) based on W = 40 (molar ratio of H_2O to AOT) at the different mass fraction of droplets (0.01, 0.04, 0.07, 0.1) . The autocorrelation function of water droplets was obtained by the DLS technique [28]. The correlation function versus

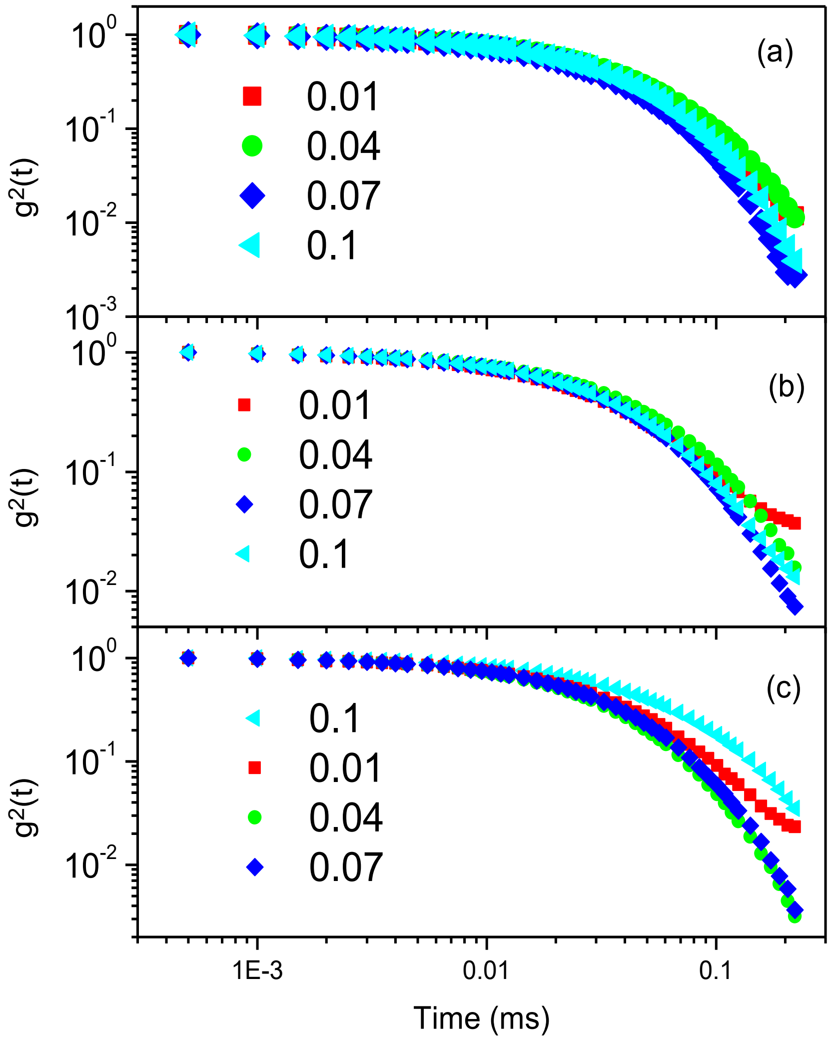

Fig. 2. The autocorrelation function versus time for AOT droplets at the different D-(+)-Glucose concentrations (a) 0.001,(b) 0.00025 and (c) 0.0000625 at RT.

decay time for AOT droplets containing D-(+)-Glucose different concentrations is presented in the Fig. 2.

To achieve the decay rate, the autocorrelation function of AOT water nano-droplets was fitted with a the single exponential function and finally the collective diffusion of AOT nano-micelles was calculated using the relation (2) [17-19,28]. The collective diffusion versus droplet mass fraction of the AOT nano-droplets comprising the different D-(+)-Glucose concentrations is shown in Fig. 3.

As observed from the Fig. 3, slope of the collective diffusion vs the mass fraction of droplet curve is positive for the AOT water droplets containing the D-(+)-Glucose with 0.001 concentration (high concentration), whereas it for the AOT RM containing the D-(+)-Glucose at the low concentration (0.0000625) is negative. In other words, the inter-nanomicelle interactions changed from attractive to repulsive as concentration of the D-(+)-Glucose monosaccharide in the water-in-oil microemulsion increased as a function of MFD.

It is important to note that the inter-nanodroplet interactions are described by a potential comprising both attractive and repulsive characters [3]. The repulsive interactions of nano-sized water droplet phase are described by a hard-sphere potential [3]. On the other hand, the attractive potential between water nano-droplets is introduced due to London-van der Waals forces [3].

The average size of AOT droplets was determined at the constant water content by converting the diffusion coefficients into hydrodynamic diameter by using the Stokes-Einstein relation (Fig. 4).

It is clear from Fig. 4, that the hydrodynamic diameter of water nano-droplets decreases as concentration of D-(+)-Glucose increases as a function of MFD.

To explain these observations can be said that: (i) D-(+)-Glucose may partly has played the role of co-surfactant in the water-in-oil AOT microemulsions [19-20]. As a result, the interfacial area of reverse micelle system has changed with increasing hydrophilic D-(+)-Glucose in the AOT micelles. So, the number of droplets increases, and then their size decreases as observed experimentally. (ii) The some parts of D-(+)-Glucose or their ends may be adsorbed at the H_2O/AOT interface, and nano-adsorbing the rest of the D-(+)-Glucose in core of AOT water droplets. So , the elastic energy of the D-(+)-Glucose monosaccharide causes the droplet size decreases [19-20]. (iii) Reduction in size of droplets also was attributed to decrease in the overlapping of the interface domain of

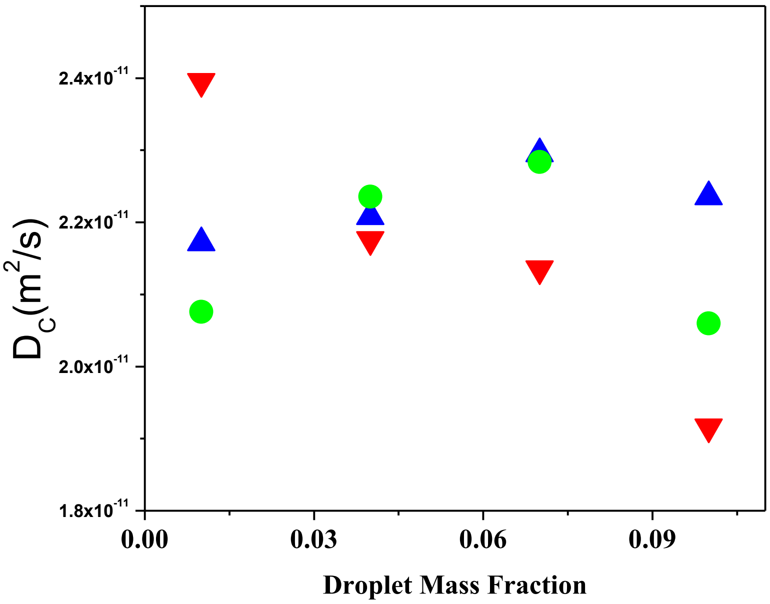

Fig. 3. Collective Diffusion Coefficient versus droplet mass fraction of AOT droplets containing D-(+)-Glucose different concentrations (down triangle): 0.0000625 (up triangle): 0.001 and (circle): 0.00025 at RT.

inter- droplets, which it can be account for change in interaction from attractive to repulsive as a result of increasing concentration of the D-(+)-Glucose monosaccharide in the water-in-oil microemulsion[19-20]. On the other hand, reduction in size of AOT droplets was assigned to increase in bending rigidity of the water/surfactant interface due to the surface-to-volume effects [19-20]. In other words, the structure and size of nano-sized water droplets are affected from the electrostatic interactions of head groups of AOT surfactant at different D-(+)-Glucose concentrations as a function of MFD [3].

It is important to note that change in the droplet size and inter-droplet interactions thus varying the content of oil in the RM system has been reported in literature [22].

The size distribution characterization of nano-droplets confirmed by dynamic Light scattering technique. The size distribution by number mode for the different AOT droplets from DLS technique is shown in Fig. 5 and Fig. 6 at RT.

Polydispersity (PDI) in size of water-nanodroplets was observed as a result of change in the concentration of D-(+)-Glucose monosaccharide and MFD in the water-in-oil AOT

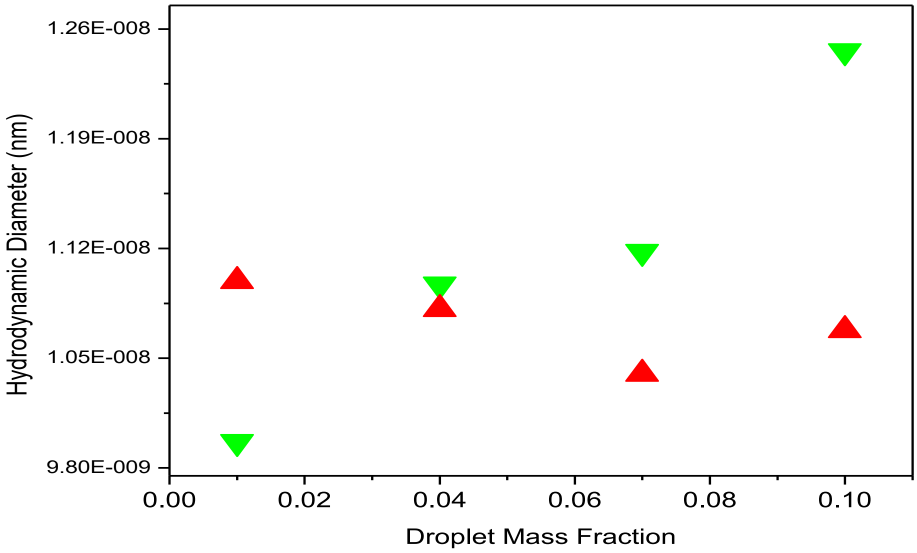

Fig. 4. Hydrodynamic diameter versus droplet mass fraction for AOT droplets containing D-(+)-Glucose different concentrations (down triangle): 0.0000625 (up triangle): 0.001 at RT.

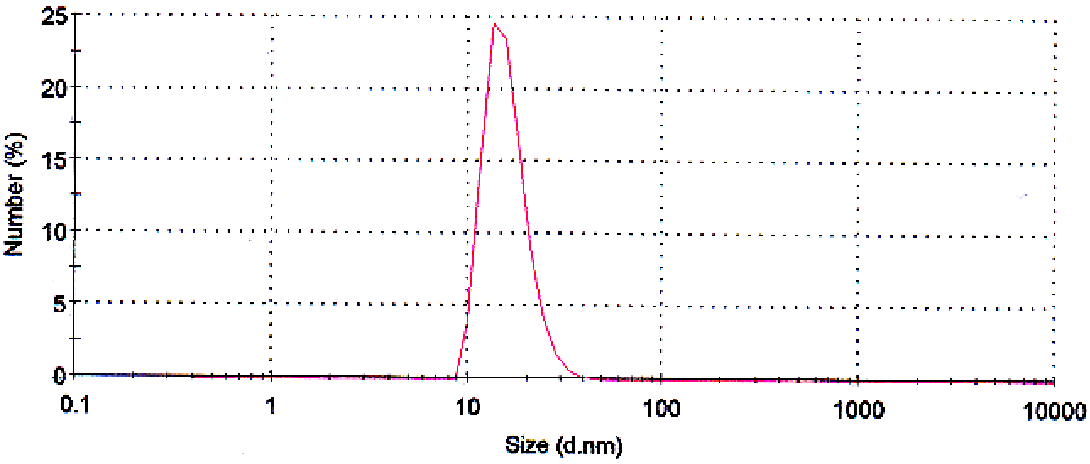

Fig. 5.Size Distribution by number of AOT droplets containing D-(+)-Glucose at the 0.001 concentration at MFD= 0.07 at RT.

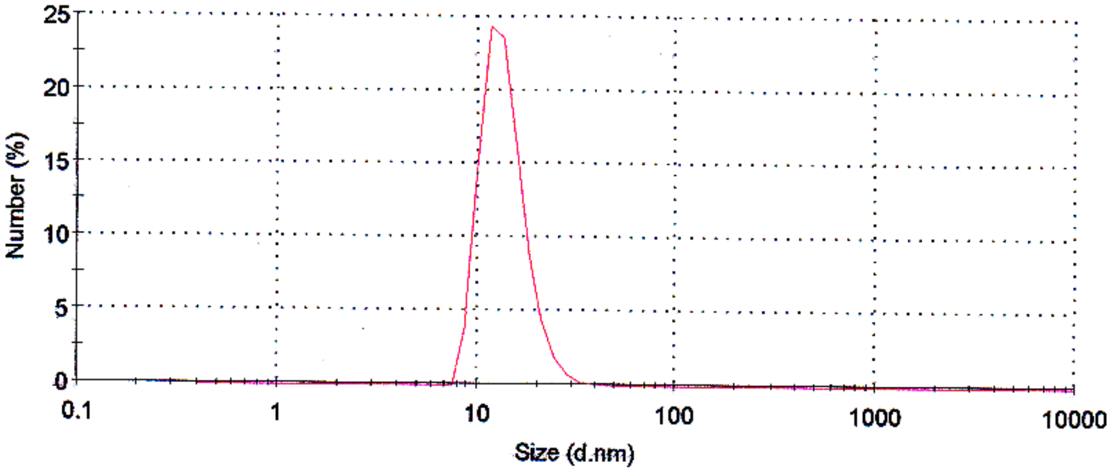

Fig. 6. Size Distribution by number of AOT droplets containing D-(+)-Glucose at the 0.001 concentration at MFD= 0.04 at RT.

microemulsion.

CONCLUSION

The collective diffusion coefficient of nano-sized droplets containing of D-(+)-Glucose different concentrations was studied. For the different D-(+)-Glucose concentrations in the water-in-oil microemulsion , a the single relaxation curve was observed for the AOT droplets. Study of dynamic light scattering of AOT droplets indicated that the diffusion coefficient of water nano- droplets increased and their size decreased as concentration of D-(+)-Glucose in the inverse microemulsion increased. Our results showed that the interaction between droplets changed from attractive to repulsive as concentration of D-(+)-Glucose in AOT droplets increased.

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CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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