Journal of Quantitative Spectroscopy & Radiative Transfer 202 (2017) 168–175

Contents lists available at ScienceDirect

Journal of Quantitative Spectroscopy & Radiative Transfer

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

Evolution of radius and light scattering properties of single drying microdroplets of colloidal suspension

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ARTICLE INFO

Article history:
Received 14 June 2017
Revised 4 August 2017
Accepted 4 August 2017
Available online 5 August 2017

Keywords:
Elastic light scattering
Microdroplet evaporation
Electrodynamic levitation
Sodium dodecyl sulfate
Silica nanospheres
Aggregation

ABSTRACT

We report on observation of well-pronounced characteristic features of elastic light scattering of evaporating solution and suspension microdroplet of the anionic surfactant sodium dodecyl sulfate (SDS) and colloidal silica (SiO_2) nanospheres in diethylene glycol (DEG) during SDS surface layer and structure formation (crystallization). For pure DEG/SDS solution droplet evaporation process, characteristic evaporation transitions manifested in the evolution of the droplet radius, $a(t)$ for all the SDS concentrations (C = 20 mM, 40 mM and 100 mM) studied as well as well-pronounced intensity signals characterizing SDS soft gel-solid transitions for initial SDS concentrations, C > 40 mM. In the case of microdroplets composed of DEG/SDS with controlled addition of colloidal silica, the intensity fluctuations were enhanced and had profiles dependent on the initial composition of the suspension. Exemplary wet droplets at the initial evaporation stages and final dry aggregates of SDS and SDS/SiO_2 were deposited on a substrate and observed with Scanning Electron Microscopy (SEM). Features of the deposited structures correlate well with the elastic scattered light measurements characterizing the drying processes.

1. Introduction

Evaporation of microdroplets containing dispersed particles or dissolved materials exhibit pronounced complex optical and thermodynamic properties [1–6] as well as distinct mechanical instabilities [7] than that of the evaporation of pure liquid microdroplets. Such colloidal suspension of microdroplets represent important morphological type of scattering objects with numerous applications in research and industry [8,9]. The temporal behavior of scattered light on drying colloidal suspension or solution microdroplets depends on both the bulk and surface properties of the droplet. The interaction of the light with the droplet surface at the air-liquid/solid interface manifest in a complex way. However, since the light interacts directly with the surface layer of the evaporating droplet, an inverse inference of the droplets' surface properties, dry microobject morphology as well as phase transitions at the droplet surface during the evaporation/drying processes can be obtained from the total distribution and evolution of the scattered light intensities.

Sodium dodecyl sulfate (SDS) is perhaps the most widely studied anionic surfactant used in both industrial products and for fundamental scientific research. For example, it has been used to simulate the behavior of surfactants observed in the atmosphere in the form of aerosol droplets [10] and is observed to posses several crystalline phases under variable temperature conditions [11]. Doganci et al. [12] studied the effects of SDS concentration on the evaporation rate of droplets placed on TEFLON-FEP substrate. In their classic work, they observed that the addition of SDS did not alter the drop evaporation rate within the first 20 min of the evaporation process. They additionally concluded that the main difference was found to be the change of the mode of the drop evaporation on the substrate including contact angle, and area variations when they varied the SDS concentrations in the droplet. However, the presence of substrate via such method can sometimes mar the final morphology of the dried products from the evaporation process.

Static and dynamic light scattering methods including quasi-elastic light scattering [13], small-angle neutron scattering [14,15], infrared spectroscopic technique [11] and many others mentioned in [11] have been used to characterize other specific physical properties of SDS. However, elastically scattered light diagnostics characterizing gradual crystallization of SDS and structure evolutions from single levitating microdroplet composed of SDS with/without other submicron inclusions have not been studied.

Here, we present a systematic study of elastically scattered light intensities characterizing the formation of crystallized SDS microstructures and SDS/SiO_2 composite micro objects from single evaporating microdroplet of solution and suspension respec-

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http://dx.doi.org/10.1016/j.jqsrt.2017.08.004
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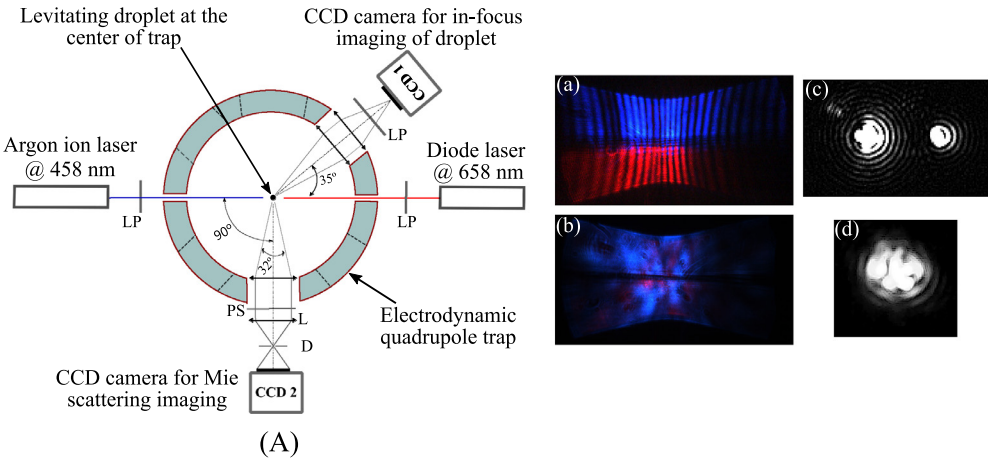

Fig. 1. Scheme showing the optical arrangement of the electrodynamic quadrupole trap (A). LP: linear polarizers, PS: polarization sheet plate, L: Lenses, CCD 1 and CCD 2 are cameras used for the in-focus imaging and Mie scattering imaging respectively. Right : Images of out-of-focus interference patterns (a, b) and in focus glare spots (c, d) observed during the microdroplet evaporation process.

tively. In particular, we examine the changes in the integrated Mie scattering vs time evolution and measure the droplet radius on the basis of Mie scattering theory [16] and by electrical weighting of the droplet position [17]. It is important to note here that, the combination of these two complementary methods of droplet size measurement technique (i.e. optical (interferometric) and weighting) enabled very accurate determination of the entire droplet/aggregate radius evolution. Weighting becomes particularly indispensable, when the elastic scattering pattern loses its regular structure, and the determination of droplet size using the interferometric method becomes compromised [10,18] or impossible. Additionally, a parallel experimental setup [19] was used to deposit exemplary initial wet aggregates (patterns) and final dry structures on a substrate and analyzed further with Scanning Electron Microscopy (SEM) to complement the observed elastic scattered light measurements.

2. Experimental section

2.1. Experimental materials and sample preparation

The sample materials used for the experiment includes: monodispersed colloidal silica nanospheres (SiO_2; 125 nm radius, refractive index = 1.465, C-SIO-0.25, Corpuscular Inc.) diethylene glycol (DEG : refractive index = 1.446, 99.0% GC area, BioUltra, Fluka, Sigma-Aldrich) and sodium dodecyl sulfate (SDS: refractive index = 1.461, ACS Reagent, $\geq$ 99:0% , Sigma-Aldrich). For the DEG/SDS solution droplet experiments, different molar concentrations of SDS at 20 mM, 40 mM, and 100 mM were prepared by mixing weighted SDS with DEG in an insulin syringe, followed by ultrasonication to obtain uniform mixing. In the case of the DEG/SiO_2/H_2O/SDS suspension droplet experiment, an initial approximate mixing ratio of DEG : H_2O : SiO_2 = 1 : 3 : 56 by volume was prepared and successive percentages by mass of SDS was added to the mixture and sonicated to obtain uniform mixing. The prepared liquid solution and suspension mixtures were carefully transferred into the droplet on-demand injector under controlled dust free environment to prevent contamination of the samples during the liquid transfer process.

2.2. Experimental setup and procedure

A schematic of the electrodynamic quadrupole trap showing the optical arrangement of the major peripherals is presented in Fig. 1A. Detailed description is given elsewhere in [3,4,20]. The trap system and its component are placed in a climatic chamber with eight side ports for optical access to the trap center. The trap and its auxiliary components are thermally regulated by a circulating liquid from an external gas-liquid heat thermostatic bath. Usually, the temperature in the climatic chamber (trap environment) is maintained at 22 $\pm$ 0.15 °C. Additionally, dry nitrogen is provided to the chamber through a gas-liquid heat exchanger to provide dry atmospheric conditions in the trap with relative humidity of not more than 5 $\pm$ 3.5% during all the experimental procedures. A droplet suspended at the center of the trap is simultaneously illuminated by a horizontally (H) polarized diode laser (658 nm; 10 mW) and vertically (V) polarized argon ion laser (458 nm; 12 mW) with respect to the scattering plane. The light scattered by the droplet is monitored and recorded by a CCD camera (CCD 2) placed at the right angle of the scattering plane at a scattering angular range of $\phi = 90 \pm 16°$ (azimuth) and $\theta = 0 \pm 5°$ (elevation). The scattered light passes through a polarization sheet (PS) that maps the horizontal polarization of the scattered light to the scattering plane in the lower half of the camera and vertical to the plane in the upper half of the camera (see Fig. 1(a)). Fig. 1(a)–(d) show respectively the out-of-focus angularly resolved Mie scattering interference patterns and in-focus images captured from the evaporation of microdroplet composed of DEG/SiO_2/H_2O colloidal suspension. In Fig. 1(a), characteristic, almost equidistant regular Mie interference patterns on both the vertical (upper half) and horizontal (lower half) polarization channels can be seen at the beginning of the evaporation process.

The patterns can be ascribed to the interference between the reflected laser light from the surface and the refracted laser light from the inner surface of the droplet. The reflected and refracted lights manifest in the in-focus image as the two horizontally displaced glare spots (Fig. 1(c)) appearing at the droplet equator [21] and is observed with the CCD 1. In our case, the in-focused image provided by CCD 1 is used to balance the weight of the droplet levitating at the center of the trap. From the image, we calculate the position of the center of light distribution (similar to center of mass) and use one of the coordinates as feedback to a PID-type loop software controller that provides a DC loop voltage to stabilize the droplet position at the center of the trap. The stabilizing DC loop voltage is recorded in synchronous with the Mie interference patterns for the entire droplet/aggregate evolution allowing comparable droplet mass-to-charge ($\frac{m}{q}$) ratio evolution and subsequently the droplet radius evolution via the weighting signal (droplet mass, $m(t)$ evolution) [17].